International Atomic Weights

Element	Symbol	Atomic number	Atomic weight	Element	Symbol	Atomic number	Atomic weight
Actinium	Ac	89	227	Molybdenum	Mo	42	95.95
Aluminum	Al	13	26.97	Neodymium	Nd	60	144.27
Americium	Am	95	(241)	Neon	Ne	10	20.183
Antimony	Sb	51	121.76	Neptunium	Np	93	(237)
Argon	A	18	39.944	Nickel	Ni	28	58.69
Arsenic	As	33	74.91	Niobium	Nb	41	92.91
Astatine	At	85	(211)	Nitrogen	N	7	14.008
Barium	Ba	56	137.36	Osmium	Os	76	190.2
Berkelium	Bk	97	(243)	Oxygen	O	8	16.0000
Beryllium	Be	4	9.013	Palladium	Pd	46	106.7
Bismuth	Bi	83	209.00	Phosphorus	P	15	30.98
Boron	B	5	10.82	Platinum	Pt	78	195.23
Bromine	Br	35	79.916	Plutonium	Pu	94	(239)
Cadmium	Cd	48	112.41	Polonium	Po	84	210
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Californium	Cf	98	(244)	Praseodymium	Pr	59	140.92
Carbon	C	6	12.010	Promethium	Pm	61	(147)
Cerium	Ce	58	140.13	Protactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium (see Niobium)				Rubidium	Rb	37	85.48
				Ruthenium	Ru	44	101.7
Copper	Cu	29	63.54	Samarium	Sm	62	150.43
Curium	Cm	96	(242)	Scandium	Sc	21	45.10
Dysprosium	Dy	66	162.46	Selenium	Se	34	78.96
Erbium	Er	68	167.2	Silicon	Si	14	28.06
Europium	Eu	63	152.0	Silver	Ag	47	107.880
Fluorine	F	9	19.00	Sodium	Na	11	22.997
Francium	Fr	87	(223)	Strontium	Sr	38	87.63
Gadolinium	Gd	64	156.9	Sulfur	S	16	32.066
Gallium	Ga	31	69.72	Tantalum	Ta	73	180.88
Germanium	Ge	32	72.60	Technetium	Tc	43	(99)
Gold	Au	79	197.2	Tellurium	Te	52	127.61
Hafnium	Hf	72	178.6	Terbium	Tb	65	159.2
Helium	He	2	4.003	Thallium	Tl	81	204.39
Holmium	Ho	67	164.94	Thorium	Th	90	232.12
Hydrogen	H	1	1.0080	Thulium	Tm	69	169.4
Indium	In	49	114.76	Tin	Sn	50	118.70
Iodine	I	53	126.92	Titanium	Ti	22	47.90
Iridium	Ir	77	193.1	Tungsten	W	74	183.92
Iron	Fe	26	55.85	Uranium	U	92	238.07
Krypton	Kr	36	83.7	Vanadium	V	23	50.95
Lanthanum	La	57	138.92	Wolfram (see Tungsten)			
Lead	Pb	82	207.21				
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutetium	Lu	71	174.99	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.22

Numbers in parentheses are for mass number of most stable known isotope.

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GENERAL CHEMISTRY

General Chemistry

WILLIAM A. FELSING

GEORGE W. WATT

Professor of Chemistry, The University of Texas

Third Edition

New York Toronto London

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1951

GENERAL CHEMISTRY

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PERHAPS THE MOST VALUABLE RESULT OF all education is the ability to make yourself do the thing you have to do, when it ought to be done, whether you like it or not; it is the first lesson that ought to be learned; and however early a man's training begins, it is probably the last lesson that he learns thoroughly.

—*Thomas Henry Huxley*

PREFACE

For those teachers who favor the trend toward greater emphasis on fundamental principles in the elementary course in chemistry, the present volume should constitute a distinct improvement over the second edition of this book. In a broad sense, the changes that have been made during the preparation of the present edition are such as to provide a more rigorous course of study with particular emphasis upon the quantitative aspects of the subject.

Extensive reorganization of order of presentation of much of the subject matter has been effected with a view to improvement in instructional methods and the scheduling of the related laboratory work.

Among the changes that have been made, the following are considered to be of major importance: The subject matter relating to atomic structure is presented much earlier, although the correlating study of the periodic arrangement of the elements is deferred until the student can become more aware of the purpose that it serves. The sections concerned with combining weights and atomic weights have been completely revised, and the concept of chemical equivalence is introduced early and given special emphasis. A considerably more rigorous treatment of chemical equilibria is provided, and the treatment of oxidation-reduction reactions has been extensively modified. The discussion of nuclear chemistry is deferred until relatively late and has been modernized and freed of some of the restrictions that were unavoidable at the time the second edition was written. Only minor changes have been incorporated in the more descriptive chapters, including those concerned with organic chemistry.

With but very few exceptions, the exercises at the ends of the chapters have been subdivided into general exercises and problems. The number and variety of problems have been greatly expanded and numerical answers are included in the back of the book. The various types of calculations are continuingly reviewed throughout the sections that otherwise deal largely with descriptive subject matter, again including the sections on organic chemistry.

The authors wish to acknowledge assistance in the form of many helpful suggestions that have been received from teachers in other institutions who have used the second edition of this book. Similar

contributions have also been made by Professors P. S. Bailey, J. R. Dice, F. H. Field, L. O. Morgan, R. M. Roberts, and R. C. Thompson, of this university, and Professor S. H. Lee of the University of Oklahoma. Special thanks are due Professor Norman Hackerman, who has given generously of his time in reading much of the manuscript and who has offered many constructive suggestions.

WILLIAM A. FELSING
GEORGE W. WATT

AUSTIN, TEX.
March, 1951

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CHAPTER 1
FORMS OF MATTER

The present state of development of the physical and the biological sciences is the result of man's effort to understand the nature of his environment and its multitude of complex changes. Rapid progress in these specialized fields of knowledge constitutes the single most important factor contributing to the increasing complexity of modern civilization. Consequently, a knowledge, or at least an appreciation, of these fields of human endeavor is an essential possession of any intelligent member of modern society. The course of study outlined in this book is an effort at the presentation of certain fundamental aspects of the science of chemistry, its methods, accomplishments, and aims.

Among the experimental sciences, chemistry and physics occupy a unique position. Their sphere of influence embraces all of the other physical sciences and exerts far-reaching influence upon the biological and even the social sciences. The steadily increasing importance of a knowledge of chemistry has prompted medical educators to require greater and greater emphasis upon the study of this subject in pre-medical curricula as well as in medical schools. Much the same situation prevails with regard to pharmacy, biology, bacteriology, etc. In different degrees, the various phases of engineering, geology, agriculture, etc., present problems which can be solved to best advantage on the basis of at least a limited knowledge of chemistry.

1.1. Nature and Scope of the Science of Chemistry

Chemistry is that branch of the physical sciences which is concerned with the composition of matter and with those transformations which matter undergoes. All objects in the material universe are suitable subjects upon which the interests of the chemist may be focused. Chemistry deals also with energy, since transformations of matter are accompanied by energy changes.

Largely as a matter of convenience, chemistry has come to be thought of as being made up of certain branches or subdivisions. It must be recognized, however, that this sort of classification is quite

arbitrary and somewhat artificial. *Inorganic chemistry* is concerned with substances that have their origin in or are commonly associated with the mineral world, *e.g.*, rocks, ores, the soil, the constituents of the atmosphere, etc. *Organic chemistry* is usually defined as the chemistry of substances that contain carbon, but this designation is not an altogether satisfactory one. *Analytical chemistry* deals with the methods by means of which the chemist can determine the composition of the various forms of matter, whether inorganic or organic. *Physical chemistry* is concerned with the various principles, laws, and theories that enable the chemist to interpret and explain the results of experiments and observations. By virtue of the very nature of its subject matter, physical chemistry becomes an essential part of each of the other branches of chemistry. Each of the four branches referred to above may be and frequently is subdivided further, but since all of these arbitrary subdivisions overlap one another and are so interdependent, it is preferable that the science of chemistry be thought of as a composite whole.

1.2. The Method of Science

It must be recognized at the outset that chemistry is based upon *experiment*. In solving the many problems with which the chemist is faced, a fairly well-defined plan of attack is usually followed. The first step involves experimentation in the laboratory and the systematic recording of observations and experimental data. Following this collecting of information, the chemist must organize the results of his experiments and examine them with a view to discovering any general relationships, principles, or laws in terms of which the observed phenomena may be described. Next, an effort is made to devise suitable theories by means of which the observed facts may be explained satisfactorily. Finally, these theories are applied in the prediction of the behavior of substances not previously studied. Here the objective is the expansion of knowledge and substantiation or disproof of the validity of theories. Such theories are of value not only because they serve in the explanation and understanding of known facts but also because theories frequently suggest lines of investigation that lead to the discovery of new truths.

1.3. Classification of Matter According to Physical State

Because the science of chemistry is concerned with matter in all of its multitude of different forms, simplification for purposes of study requires that every effort be made to organize and classify the materials

involved. Initial efforts at classification may achieve only a gross segregation of matter into broad types, each of which upon further study may have to be divided further into numerous subtypes. Two very broad classifications are indicated in the following paragraphs.

Everyone is aware of the fact that water, which is ordinarily a liquid, may also exist in the form of a gas (steam) or as a solid (ice). Since many other substances are capable of existing in all three of these states of aggregation and since all known forms of matter exist in at least one, it becomes convenient to classify matter according to the three physical states, *viz.*, *solid*, *liquid*, and *gas*. The characteristics of matter as it exists in these conditions are considered elsewhere in this and in subsequent chapters.

1.4. Classification of Matter According to Composition

A somewhat more involved but nevertheless useful classification of matter may be made in terms of composition. Any object may be classified under one of the three headings: *element*, *compound*, or *mixture*. This classification is by no means so simple as that based on physical state. This fact becomes apparent when one realizes that matter in all the physical states is encountered in each of the three groupings according to composition. Because all the materials encountered in the study of chemistry are classified (according to composition) as elements, compounds, and mixtures, it is essential that the characteristics of each and the distinctions among the three be understood thoroughly. Consequently, each is considered here in some detail.

The student who would learn of chemistry must appreciate the fact that the study of a science involves, in some measure, the same tasks as are encountered in the study of a language. One cannot hope to read, write, or speak a foreign language without first acquiring an adequate vocabulary; neither can one progress in the study of a science without learning the vocabulary that permits one to speak fluently and think in terms of the language of that particular science. From the beginning, therefore, the student should pay particular attention to the exact meaning of terms employed and to distinctions between related terms.

1.5. Elements

Suppose that a sample of ordinary table salt is studied in the laboratory with a view to breaking the salt down into its constituent parts. It is found by experiment that the white solid salt may be decom-

posed into two simpler substances. One of the products of this decomposition is a greenish-yellow gas known as *chlorine;* the other is a soft metallic solid known as *sodium.* The object of the experiment has been realized since it has been demonstrated that table salt is composed of two simple substances. Further experiments must now be performed to determine whether the sodium, the chlorine, or both can be decomposed still further. It is found that such is not possible by any ordinary means. Another approach to this problem lies in the chance that, even though it is not possible to decompose sodium or chlorine, one might hope to produce sodium or chlorine by bringing together other materials of a more elementary character. Here again, all efforts would be met by failure. The inescapable conclusion, therefore, is that sodium and chlorine must be of elemental nature, *i.e.*, they must be substances that should be classified as elements. **An element is a substance that cannot by any ordinary means be built up from or decomposed into simpler substances.**

The Number and Kinds of Elements. At the middle of the eighteenth century only about 17 elements were definitely known, but by 1890 the number was increased to about 70. At present the identity of 98 elements is firmly established. The question as to the maximum possible number of elements has been and continues to be the object of much speculation.

Elements may be classed, roughly, into two groups: *metals* and *nonmetals.* The nonmetals constitute more than one-half of the total weight of the earth's crust and include such substances as oxygen, sulfur, carbon, nitrogen, and chlorine. Among the metals found in the earth's crust are such common materials as iron, lead, zinc, copper, aluminum, silver, and gold. Only about one-half of the known elements are usually encountered by the chemist in his work; only rarely does he see or work with the others. The earth's crust together with the sea and the atmosphere is composed largely of 12 elements: oxygen, silicon, aluminum, iron, calcium, magnesium, sodium, potassium, hydrogen, titanium, carbon, and chlorine. Of these, oxygen is by far the most abundant.

1.6. Properties of Substances

If one should be asked to identify two automobiles made by different manufacturers, the distinction between the two could probably be made readily in terms of gross differences in appearance. However, if it became necessary to identify two different makes of automobile produced by the same manufacturer, these two might be so similar

that a more careful examination would be required. In any event, there could be found at least enough minor differences to distinguish the one from the other. This same type of problem is involved in the study of chemistry. One of the first tasks that faces the student is that of recognizing certain chemical substances. Each substance has certain characteristics which are usually called *properties*. Thus, ordinary window glass has certain well-defined properties such as hardness, transparency, and ease of fracture. Sulfur is an element having self-evident properties such as color, odor, and taste. **The properties of a substance are those attributes or characteristics in terms of which that substance may be recognized or identified.**

1.7. Compounds

The elements sulfur and lead have properties by which they may be recognized without difficulty. If lead and sulfur are heated together, there is produced a new substance having properties that are very different from those of lead or sulfur. The product of this chemical union is known as *lead sulfide* and is a *compound* containing the elements lead and sulfur. The following conclusions may be drawn from this simple experiment: (1) the union of two simple substances (elements) resulted in the formation of a more complex substance (a compound); (2) upon entering into chemical union the characteristic properties of the two elements disappeared, and a new substance having its own set of characteristic properties was produced. On the basis of this and other similar experiments it is possible to arrive at a satisfactory definition of the term *compound*. **A compound is a substance formed from two or more elements. The properties of a compound are different from those of its constituent elements.**

Synthesis and Analysis. The process of producing more complex substances by the union of two or more simple substances is known as *synthesis*. Thus, the synthesis of lead sulfide is accomplished by the union of lead and sulfur. Similarly, the compound known as *water* may be synthesized by the combination of the elements hydrogen and oxygen. The use of the term synthesis is not restricted to the cases involving the union of elements but is also applied commonly, for example, to the union of two or more compounds to form another more complex compound.

The laboratory examination of a substance for the purpose of determining its composition is termed an *analysis*. When a sample of an ore, for example, is sent to a chemical laboratory for analysis, the sender wishes the chemist to examine it for the purpose of finding out

what it contains. If the analysis is made only for the purpose of determining the identity of the substances involved, the analysis is said to be *qualitative*. Thus a qualitative analysis of an iron ore might show that the ore consists of iron and oxygen. The analysis might, however, be so conducted as to yield information as to the quantities of iron and oxygen present in the ore; such an analysis is termed a *quantitative analysis* and might supply the information, for example, that the ore contains 69.9 per cent of iron and 30.1 per cent of oxygen.

1.8. Law of Definite Proportions

The simple fact that a chemical compound consists of two or more elements provides no information as to the quantities of the elements concerned. Suppose that samples of table salt, which is a compound known as *sodium chloride*, are obtained from various parts of the world and purified in order to make certain that every sample is entirely free of impurities. If one of these samples, weighing 1 lb., is subjected to a quantitative chemical analysis, it is found that the 1 lb. of sodium chloride consists of 0.3934 lb. of sodium and 0.6066 lb. of chlorine. The analysis of another sample of pure sodium chloride from an entirely different source would lead to exactly the same result. Finally, after all the samples are analyzed, it is found that the results are identical, or as nearly so as the accuracy of the experimental method permits. After similar experiments using a wide variety of pure compounds, the conclusions drawn from this experience may be summarized in an expression known as the *law of definite proportions* or sometimes as the *law of constant composition:* **The composition of a pure compound is always precisely the same.**

1.9. Physical and Chemical Changes

The transformations of matter referred to in the preceding paragraphs fall into two distinct classes. The melting of solid ice and the formation of ice from liquid water are examples of *physical change*. It is a well-known fact that a bar of steel may be magnetized and may thereafter behave as a magnet for an indefinite period of time. This also is an example of a physical change. It is of importance to recognize that the chemical composition of the bar of steel was not altered in the process of magnetization; neither did any change in composition result from the transformation of solid water to liquid water. **A physical change may be defined as a transformation of matter which may be accomplished without change in chemical composition.**

The physical changes that occur when heat is applied to ice may be represented as follows:

$$\text{Ice}_{(\text{solid})} \rightarrow \text{water}_{(\text{liquid})} \rightarrow \text{steam}_{(\text{gaseous})}$$

Although most solids, when heated, melt to liquids, which upon further application of heat are converted to gases, the student should not infer that this sequence of changes of state occurs in all cases. When solid iodine, for example, is heated, the solid is changed directly to the gas.

$$\text{Iodine}_{(\text{solid})} \rightarrow \text{iodine}_{(\text{gaseous})}$$

That is, the iodine is converted to the gaseous state without first melting to a liquid. This may be demonstrated readily with the simple apparatus shown in Fig. 1. Solid iodine is placed in the bottom of the beaker and a porcelain dish filled with ice water is placed over the top of the beaker. Upon application of heat to the bottom of the beaker, purple gaseous iodine appears in the space above the solid iodine. When these vapors strike the cold undersurface of the dish, the gaseous iodine condenses to solid crystalline iodine. Such change in which a solid is converted directly to the vapor state followed by direct condensation of the vapor to the solid state is known as *sublimation*. Common physical changes together with descriptive terms employed in speaking of these changes are summarized in Table 1.

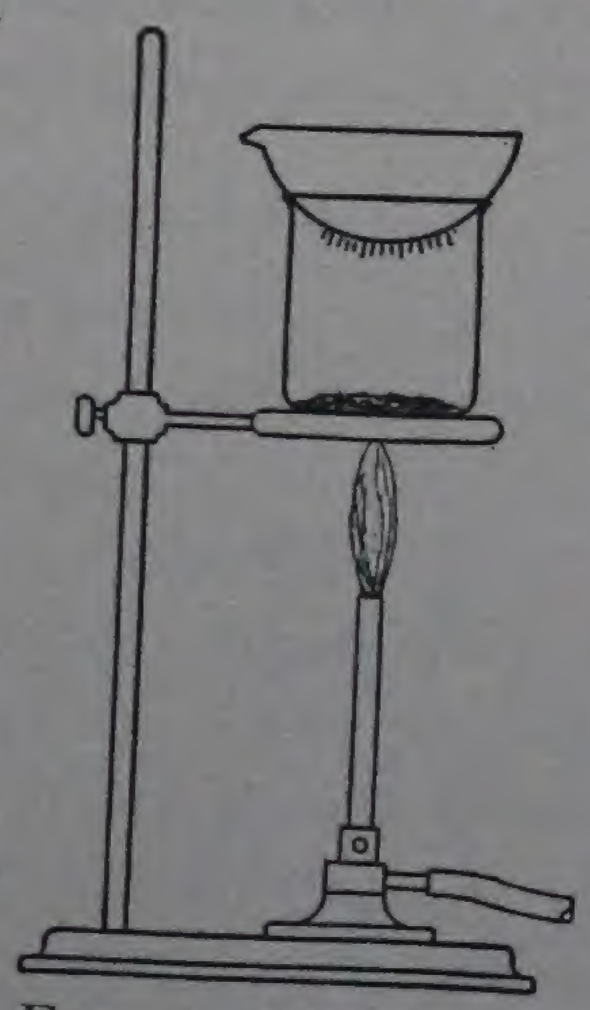

FIG. 1. Sublimation of iodine.

TABLE 1

CHANGES IN STATE

Changes	Descriptive Terms
Solid to liquid	Melting (fusion)
Liquid to gas	Boiling (vaporization, volatilization, evaporation)
Gas to liquid	Liquefaction (condensation)
Liquid to solid	Freezing (solidification)
Solid to gas	Evaporation
Solid to gas to solid	Sublimation

The decomposition of table salt has been referred to previously. Another change which may be effected easily is the decomposition of ordinary cane sugar. If white crystals of sugar are heated, the sugar caramelizes and upon further heating decomposes into carbon and water. Both of these transformations appear to involve much more

deep-seated changes than were encountered in simple physical changes. Both the table salt and the sugar have been destroyed as such and have been replaced by substances of different properties and different chemical composition. A similar situation was encountered as the result of the formation of lead sulfide by the union of lead and sulfur. **Changes in which one or more substances unite, or are decomposed, to form one or more substances having new properties are called** *chemical changes*, **or** *chemical reactions*. A chemical (or physical) change is always accompanied by an energy change.

1.10. Law of Indestructibility of Matter

By taking advantage of the possibility of determining the *weights* of materials that undergo physical or chemical change, it becomes possible to arrive at a generalization of fundamental importance. Suppose that a sample of ice weighing exactly 1 lb. is melted under such conditions that none of the resulting liquid water is lost. If the water formed is weighed accurately, it is found that from exactly 1 lb. of ice there was produced exactly 1 lb. of water. By an extension of this experiment it could be proved that from 1 lb. of water there may be produced 1 lb. of steam. It now becomes of interest to inquire as to whether a similar result is obtained from the study of a chemical change.

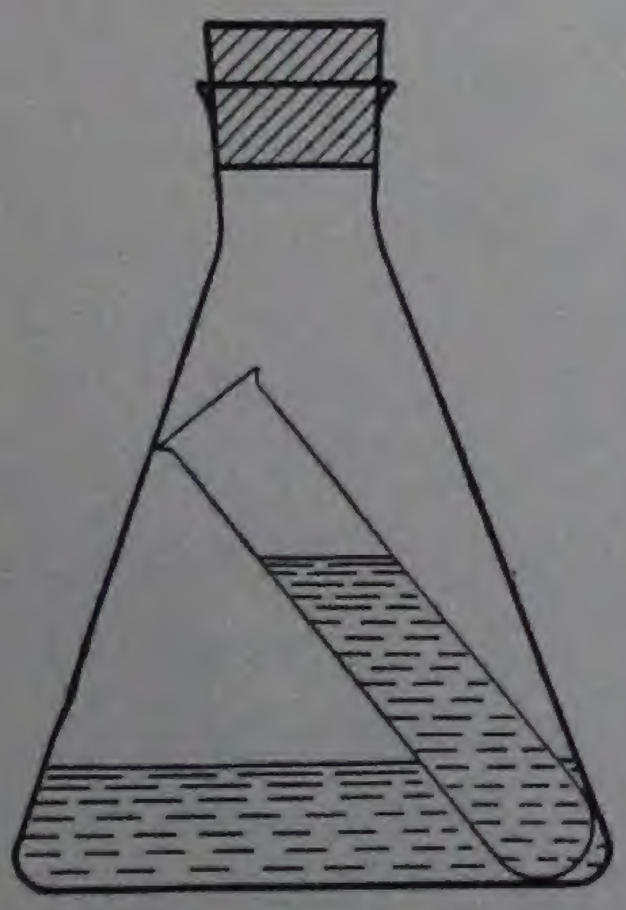

FIG. 2. Simple demonstration of the law of indestructibility of matter.

The answer to this question may be found by a very simple experiment. Into a flask (Fig. 2) containing a solution of a compound known as *potassium chromate*, there is placed a test tube containing a solution of another chemical compound called *lead nitrate*. The top of the test tube rests against the upper wall of the flask so that the two solutions are not mixed. The flask is then fitted with a tight rubber stopper and the entire assembly weighed accurately. When, without removing the stopper, the flask is inverted so that the two solutions are mixed, there occurs a chemical change in which yellow solid lead chromate is produced. For present purposes, this change may be represented as follows:

$$\underset{\text{(dissolved)}}{\text{Potassium chromate}} + \underset{\text{(dissolved)}}{\text{lead nitrate}} \rightarrow \underset{\text{(solid)}}{\text{lead chromate}} + \underset{\text{(dissolved)}}{\text{potassium nitrate}}$$

If the weight of the flask and its contents is now determined with accuracy, it is found that the weight is exactly the same as it was before the occurrence of the chemical reaction.

From the experiments described above as well as from many others, it is apparent that matter is neither destroyed nor created as the result of physical and chemical change. This fact is the basis of the law of indestructibility of matter, which may be stated as follows: **The occurrence of ordinary physical and chemical changes does not result in any change in the total weight of the materials involved.**

1.11. Mixtures

When two substances are brought together, they do not necessarily combine to form a compound. For example, if iron filings and lumps of sulfur are mixed at ordinary temperatures, chemical combination does not occur. Such a mixture is said to be *heterogeneous*, since the component parts of the mixture may be distinguished by the unaided eye. Obviously, it would be possible to separate the components of this mixture merely by picking out the iron filings with a pair of forceps. If, however, this mixture is ground to a very fine powder, the two components become so intimately mixed that the individual particles can no longer be recognized. Under these conditions, the mixture is said to be *homogeneous*.[1] If a horseshoe magnet is drawn through this homogeneous mixture, the powdered iron is attracted and held by the magnet while the particles of sulfur are not. Thus, the iron and sulfur may be separated by repeated use of the magnet. It may be concluded that the components of a mixture may be separated by purely mechanical means.

Distinction between Mixtures and Compounds. If a homogeneous or heterogeneous mixture of iron and sulfur is heated, they unite to form a compound known as *iron sulfide*. The component parts of this or any other compound cannot be separated by the use of forceps, magnets, or any other purely mechanical methods. Only by decomposition which involves chemical change can the iron and sulfur be separated and recovered in their original forms. Consequently, the mixtures and compounds differ in that mixtures can be separated into their component parts by mechanical means whereas a

[1] Care must be exercised to make clear the basis for the use of this term. A mixture that appears homogeneous to the unaided eye may be quite evidently heterogeneous when viewed under a microscope. Unless otherwise indicated, the use of the term *homogeneous* in this book implies homogeneity as judged by the unaided eye.

compound can be separated into its constituents only by the use of chemical methods.

1.12. Atomic Theory

Having recognized that the chemical elements represent relatively simple units of matter, one is led to inquire into the exact nature of these elemental substances. Historically, the concept that all matter is composed of small discrete particles dates back to the Greek philosophers who lived several centuries before Christ. Their ideas were not

FIG. 3. John Dalton (1766–1844). (*Courtesy of the Franklin Institute.*)

based upon any experimental evidence since they believed experimentation to be beneath their dignity. Nevertheless, these ideas as to the particulate character of matter persisted down through the centuries even without any quantitative experimental basis. In 1804, the English chemist John Dalton (Fig. 3), in an effort to explain such fundamental laws as the law of indestructibility of matter and the law of definite proportions, revived and extended these concepts to the extent of presenting a rather complete picture as to how he believed chemical combination occurred. This theory, which has come to be known as *Dalton's atomic theory*, embraced many erroneous ideas which have long since been discarded. The essential and useful features of

this atomic theory in a somewhat modified form may be summarized as follows:

1. Each element is made up of small particles called *atoms*.
2. The atoms of a given element have the same weight and are identical in every respect.
3. Atoms of different elements are dissimilar and have different weights.
4. During chemical or physical change, atoms are not subdivided.
5. Atoms have the ability to attract other like or unlike atoms and to hold them in chemical combination.
6. Two or more atoms unite to form particles known as *molecules*.
7. Atoms combine in simple whole-number ratios, and for any pure substance the ratio is always the same.
8. Atoms of two different elements may combine in more than one ratio to form different compounds.

FIG. 4. Stanislao Cannizzaro (1826–1910). (*Courtesy of The Edgar Fahs Smith Memorial Collection in the History of Chemistry, The University of Pennsylvania.*)

In Dalton's time so little was known about the relative weights of the atoms of the different elements that the theory failed to receive the recognition that it merited. The true value of Dalton's views did not become apparent until 1860 when the Italian chemist Cannizzaro (Fig. 4) suggested a clear procedure by means of which numerical values for the relative weights of atoms might be assigned. At the present time, although scientists are fully cognizant of the significance of Dalton's early work, it must be recognized that modern knowledge requires that the theory as outlined above must be accepted only after certain further modifications. Several such modifications become apparent or are pointed out in later chapters.

Atoms and Molecules. In the light of Dalton's theory, **an atom may be defined as the smallest particle of an element capable of taking part in a chemical reaction.** If unlike atoms unite, molecules of a compound are produced. For example, atoms of the element hydrogen combine with atoms of the element oxygen and form mole-

cules of the compound known as *water*. The union of two or more atoms of the same kind, however, results in the formation of molecules of the element concerned. Thus, 2 atoms of the element oxygen unite to form a molecule of the element oxygen. The molecules of most of the elemental gases such as oxygen, hydrogen, nitrogen, and chlorine contain 2 atoms under ordinary conditions. The molecule of the element sulfur may contain 2, 4, 6, or 8 atoms; that of phosphorus usually 4, arsenic 4, etc. **A molecule is defined as the smallest unit of matter capable of a separate distinct physical existence.** On the basis of this none too satisfactory definition, the terms *atom* and *molecule* in some cases are synonymous. The atoms of the inert gases of the atmosphere (helium, neon, argon, krypton, and xenon) do not combine to form molecules. Accordingly, the atom of helium is the smallest particle of helium capable of a separate physical existence and hence qualifies under the above definition of a molecule. Similarly, most of the metals are usually considered as elements which consist of single atoms rather than molecules containing two or more atoms.

GENERAL EXERCISES

1. Define the following terms: (*a*) element, (*b*) compound, (*c*) sublimation, (*d*) atom, (*e*) molecule.
2. Distinguish between the following terms: (*a*) compound and mixture, (*b*) synthesis and analysis, (*c*) qualitative and quantitative analysis, (*d*) chemical and physical change, (*e*) homogeneous and heterogeneous mixtures, (*f*) molecules of an element and molecules of a compound.
3. State the law of indestructibility of matter.
4. State the law of definite proportions.
5. Cite two bases upon which matter may be classified.
6. Outline the essential features of Dalton's atomic theory.
7. Explain what is meant by the properties of a chemical substance.

SUGGESTED READING[1]

Journal of Chemical Education

Horn, Relation of Chemistry to Health and Disease, **4**, 711 (1927).
Haskins, The Relation of Chemistry to Agriculture, **4**, 723 (1927).
Greenhill, The Relation of Chemistry to the Development of the Cotton Industry, **4**, 743 (1927).
Rutenber, The Relation of Chemistry to National Defense, **4**, 736 (1927).
Barnsley, The Relation of Chemistry to the Home, **4**, 730 (1927).
Abel, Chemistry in Relation to Medicine, **6**, 1045 (1929).

[1] Following the name of each chemical journal to which reference is made, there is given the name of the author or authors, the title of the article, the journal volume number, page number, and year of publication. References to books include the name of the author, the title of the book, the name and address of the publisher, and the year of publication.

URBAN, The Relation of Chemistry to the Development of the Petroleum Industry, 3, 683 (1926).
MENSCHUTKIN, Historical Development of the Concept of Chemical Elements, 14, 59 (1937).
ROBERTSON, Sublimation, 9, 1713 (1932).
DAVEY, The Reality of the Atom, 4, 327 (1927).
FRENCH, The Law of Definite Proportions, 6, 1542 (1929).
DEMING, The Laws of Definite Composition and Definite Proportions, 19, 336 (1942).
COWARD, John Dalton (1766–1844), 4, 23 (1927).
PARRAVANO, Cannizzaro and the Atomic Theory, 4, 836 (1927).
ATKINSON, The Atomic Hypothesis of William Higgins, 17, 3 (1940).
VINEYARD, The Place of Theory in the Scientific Method, 26, 383 (1949).

CHAPTER 2

WEIGHT RELATIONSHIPS

Any real appreciation of the nature of chemical change can come only from a knowledge of the *quantities* of the various forms of matter involved. The law of indestructibility of matter could not have been established as a valid generalization had not the French chemist Lavoisier (Fig. 5) devised a sensitive balance and through its use proved that matter is neither created nor destroyed when chemical changes occur. Although done with equipment that was crude by comparison with that in common use at present (Fig. 6), Lavoisier's work represented the beginning of a new era. When chemists learned to study chemical reactions in terms of quantities, chemistry passed from the realm of the arts into the category of the sciences.

FIG. 5. Antoine Laurent Lavoisier (1743–1794). (*Courtesy of The Edgar Fahs Smith Memorial Collection in the History of Chemistry, The University of Pennsylvania.*)

2.1. Measurement of Weight

With but few exceptions, the chemist expresses weight in terms of grams or fractions or multiples thereof. This unit of weight, the *gram*, is the weight of a definite volume (1 ml., see Sec. 6.5) of water at a temperature of 4° on the centigrade scale.[1] The units most frequently used in chemical work are listed in Table 2; the relation between grams and pounds is included for comparison.

The term *gram* is commonly abbreviated by the letter g., which unfortunately is used also by the pharmacist as an abbreviation for

[1] This temperature scale is different from the Fahrenheit temperature scale used in the home. For an explanation of the centigrade scale and a comparison of these scales, see Sec. 5.11.

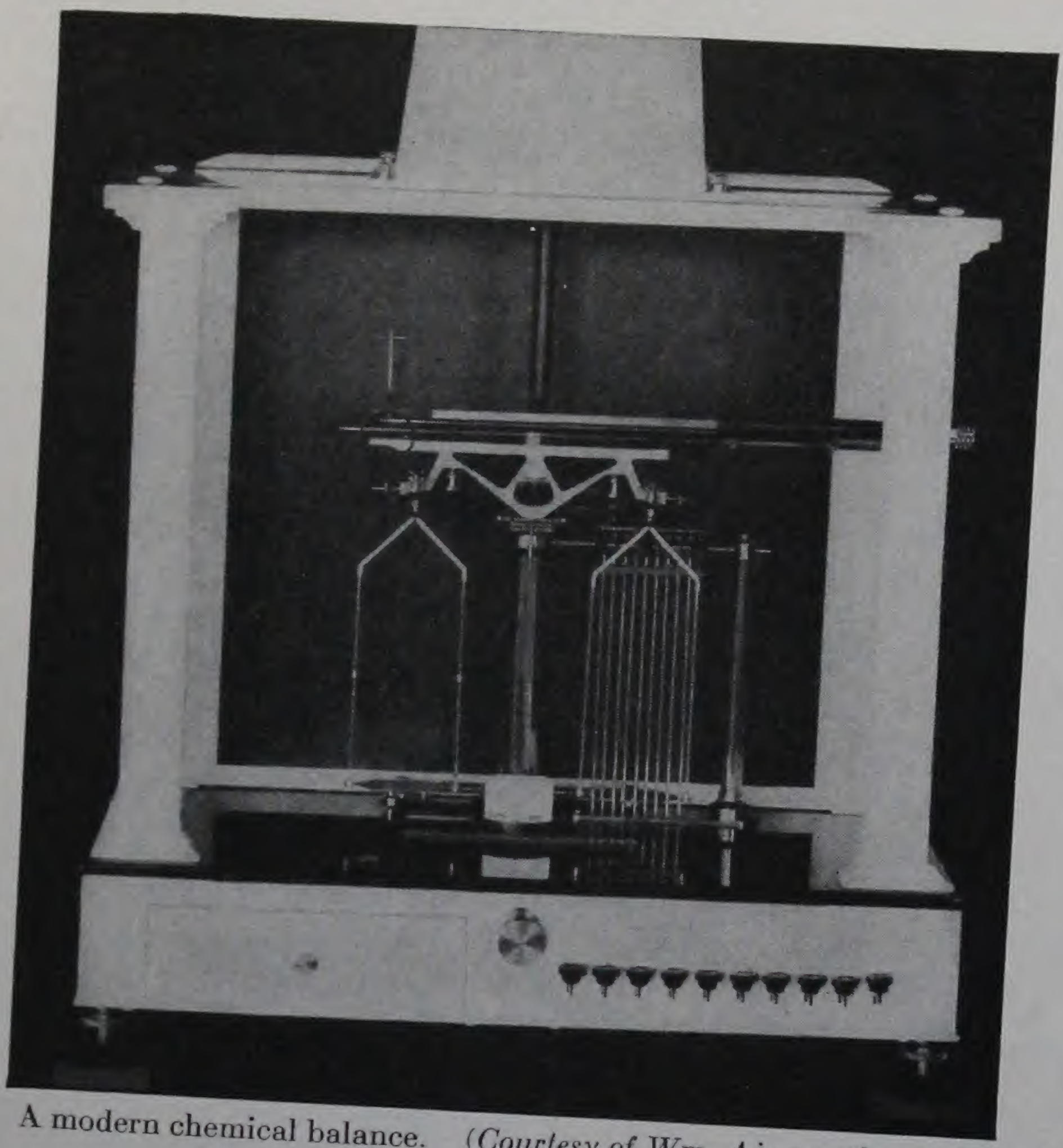

FIG. 6. A modern chemical balance. (*Courtesy of Wm. Ainsworth and Sons, Inc.*)

another unit of weight, the grain. Similarly, the abbreviations mg. and kg. are used for milligram and kilogram, respectively.

TABLE 2

UNITS USED IN THE MEASUREMENT OF WEIGHT

Unit	Designation
1 gram	Weight of 1 milliliter of water at 4°C.
1 milligram	One one-thousandth of 1 gram (0.001 g.)
1 kilogram	1000 grams
1 pound	453.59 grams

2.2. Equivalent Weights and the Law of Multiple Proportions

It has been pointed out in the preceding chapter that, according to the law of definite proportions, the elements that make up any pure compound are always present in exactly the same proportions by weight. A quantitative analysis of water, for example, shows that

pure water always consists of 8 parts by weight (grams) of oxygen and 1.008 parts by weight (grams) of hydrogen. Similarly, the compound formed by the union of hydrogen and chlorine is found to contain 1.008 g. of hydrogen combined with 35.457 g. of chlorine. Thus, in the compounds known as water and hydrogen chloride, it is evident that perfectly definite quantities of oxygen and chlorine, respectively, are in combination with a fixed weight of hydrogen (1.008 g.). It next becomes of interest to see in what ratio chlorine and oxygen combine. Analysis of the compound called chlorine monoxide leads to the striking conclusion that 35.457 g. of chlorine combines with 8 g. of oxygen. The weight relationships in these three compounds may be summarized as follows:

Compound	Element, g.		
	Oxygen	Hydrogen	Chlorine
Water	8	1.008	
Hydrogen chloride	...	1.008	35.457
Chlorine monoxide	8	.....	35.457

If this procedure is extended to include a much larger number of compounds, and if one elects to calculate the weight ratios in terms of some prearranged basis such as 8 g. of oxygen (or 1.008 g. of hydrogen), a consistent relationship is found. The quantities of the different elements that combine with 8 g. of oxygen are often the same quantities in which these different elements combine with each other. If the latter quantities are not the same as those which combine with 8 g. of oxygen, then they are simple integral multiples of those quantities. Such regularity in behavior suggests the desirability of expressing these weight relationships in terms of some one element so that there will be a common measure of things that are chemically equivalent to each other. For reasons that are explained later, 8 g. of oxygen is taken as the best possible basis, and **the equivalent weight of an element is defined as that weight which combines with eight grams of oxygen.**

An additional example serves also to focus attention upon still another complication. The compound known as nitrogen dioxide (a compound containing the elements nitrogen and oxygen) is found by analysis to consist of 69.55 per cent oxygen and 30.45 per cent nitrogen.

The equivalent weight of nitrogen in this compound is found as follows (where x represents the value sought):

$$\frac{x}{8} = \frac{30.45}{69.55}$$

$$69.55x = 8 \times 30.45$$

$$x = \frac{8 \times 30.45}{69.55}$$

$$= 3.502$$

The situation however is not quite this simple. As early as the beginning of the nineteenth century, chemists were aware of the fact that two elements may unite in different ways to form more than one compound. In addition to nitrogen dioxide, for example, the elements nitrogen and oxygen combine to form still other compounds that are representative of the class of chemical substances known as *oxides*. Some of these are listed below, together with their percentage composition as determined experimentally by quantitative chemical analysis. In the last column there is given for each compound the weight of nitrogen combined with 8 g. of oxygen (calculated as shown above), and an inspection of these values shows at once that the equivalent weight of an element is different in different compounds.

Oxide	Oxygen, %	Nitrogen, %	Equivalent weights of nitrogen
Nitrogen dioxide	69.55	30.45	3.502
Nitric oxide	53.32	46.68	7.004
Nitrous oxide	36.35	63.65	14.008

From the numbers in the last column it is clear that the weights of nitrogen that combine with 8 g. of oxygen are related one to the other as simple integral multiples. Thus, $7.004 = 2 \times 3.502$; while $14.008 = 4 \times 3.502$; and $14.008 = 2 \times 7.004$. The fact that John Dalton found this invariable relationship to hold for very many different types of chemical compounds led him to formulate the law of multiple proportions, which may be stated as follows: **The weights of any element which combine with a fixed weight of another element to form different compounds are related to each other in the ratio of small whole numbers.**

This same relationship appears in all cases in which two elements combine to form more than one compound. The metallic element chromium, for example, forms three compounds with oxygen. Listed below are the percentage compositions of these compounds and the calculated equivalent weights of chromium. Here again the interrelationship of the latter numbers is self-evident and strictly in accordance with the law of multiple proportions.

Oxide	Oxygen, %	Chromium, %	Equivalent weights of chromium
Chromium monoxide.....	23.52	76.48	26.016
Chromic oxide.....	31.57	68.43	17.344
Chromium trioxide.....	47.99	52.01	8.672

It is next shown how these facts become useful in the establishment of the numerical values which are used to represent the relative weights of the various kinds of atoms.

2.3. The Standard for Relative Atomic Weights

On the basis of the atomic theory and in view of the definition of the atom, it seems reasonable to assume that the act of chemical union of two or more elements involves the combination of atoms of those elements. If this is a true picture, then the weight relationships portrayed above must in some way be related to the weights of the atoms concerned. As is shown later, it is possible to know the actual weight, in grams, of each kind of atom. Such values, however, would be very cumbersome for use in chemical calculations and are so small as to be practically meaningless. If one wished to buy a tract of land and was told that the land under consideration consisted of 6,272,640 sq. in., the prospective buyer would have little knowledge as to the size of the tract. If, on the other hand, he was told that the tract of land consisted of 1 acre (6,272,640 sq. in.), this information would convey a real meaning. By the same token the atom is such an exceedingly small piece of matter that a number representing its true weight in grams would be so small as to carry no real significance to the human mind.

For this and other reasons, it is convenient to assign in a somewhat arbitrary manner a value representing the weight of some one kind of atom and thereafter to express the weights of other atoms in relation to this standard. Since equivalent weights were calculated in terms of 8 g. of oxygen, this immediately suggests itself as a basis for expressing

the relative weights of atoms. It must be remembered, however, that this particular quantity of oxygen is that combined with 1.008 g. of hydrogen in water. Now if the water molecule contained 1 atom of hydrogen and 1 of oxygen, then the weight of the hydrogen atom (relative to O = 8) would be 1.008. The fact is, of course, that the water molecule contains 2 atoms of hydrogen and 1 of oxygen, and the relative weight of the hydrogen atom therefore would be 0.504. Solely as a matter of convenience, it is desirable that the values for the relative weights of all kinds of atoms shall be equal to or greater than unity and that they be as nearly whole numbers as possible. Both of these requirements are met best if the number 16.0000 is chosen to represent the weight of the oxygen atom. On this basis the relative weight of the hydrogen atom (*i.e.*, the atom of the lightest element) is 1.008.

The choice of the element oxygen rather than some other element is based upon the fact that oxygen combines with nearly all of the elements to form oxides. This makes possible a direct experimental study of the weight ratios in which the different elements combine with the standard element. Otherwise, an indirect approach would have to be used. If, for example, nitrogen did not form any compound with oxygen but did form a compound with hydrogen, then one could get a value for the relative weight of the nitrogen atom (less conveniently and perhaps less accurately) in relation to H = 1.008, which is already correctly established on the basis of O = 16.0000.

From the previously calculated values for the equivalent weights of nitrogen and chromium in terms of 8 g. of oxygen, it follows that the weights of these elements which (in their specified compounds) are combined with 16 g. of oxygen are twice the values for the respective equivalent weights. *That weight of any element which combines with sixteen grams of oxygen is called a relative combining weight of that element.* Thus for nitrogen dioxide, nitric oxide, and nitrous oxide, the combining-weight values are 7.004, 14.008, and 28.016, respectively. Similarly, those for chromium monoxide, chromic oxide, and chromium trioxide are 52.032, 34.688, and 17.344, respectively. For the elements nitrogen and chromium one thereby obtains values for relative combining weights with a degree of accuracy that is limited only by the accuracy of the methods used in analyzing the compounds under consideration.

The next question that arises has to do with the relation between the relative combining weights and the relative weights of the atoms ("atomic weights") of nitrogen and chromium. It may be stated at this point that the values for the combining weights either prove to be

equal to the atomic weights or may be made equal to the atomic weights by multiplication by the ratio of two small whole numbers. The equivalent weights are similarly related to the corresponding atomic weights except that the small-whole-number ratios differ because the relative combining weights are twice as large as the equivalent weights. Before the above question is answered fully, however, some additional experimental information is necessary.

2.4. Approximate Atomic Weights

There are available certain chemical and physical methods by means of which approximate values for the atomic weights may be obtained experimentally. If the element in question is a gas, or if the element forms one or more compounds that exist as gases or volatile liquids, a value for the approximate atomic weight of the element may be had without serious experimental difficulty. For example, it may be shown by experiment that the relative weight of the nitrogen *molecule* is approximately 28. If, as pointed out earlier, the molecule of nitrogen consists of 2 atoms (Sec. 1.12), then it follows that the approximate atomic weight of nitrogen is $28 \div 2 = 14$.

Method of Dulong and Petit. For elements which are not gaseous and which do not form volatile compounds, approximate values for the atomic weights may be obtained from a knowledge of the specific heats of the elements. **The specific heat of an element is defined as the quantity of heat** (expressed in calories[1]) **required to raise the temperature of one gram of the element one degree on the centigrade temperature scale.** In 1818, Dulong and Petit discovered that, when the atomic weights of some metallic elements are multiplied by their specific heats, the products are usually numbers between 6 and 7 and that these numbers average about 6.4. Thus,

$$(\text{At. wt.}) \times (\text{specific heat}) = 6.4$$

or

$$\text{At. wt.} = \frac{6.4}{\text{specific heat}}$$

If the atomic weight is unknown and the specific heat of the particular element can be determined experimentally, it is possible to calculate the approximate atomic weight for such elements. The specific heat of chromium is found by experiment to be 0.116 calorie. Accordingly,

[1] For definition of the term *calorie*, see Sec. 5.9.

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an *approximate* value for the atomic weight of chromium may be calculated.

$$\text{At. wt.} = \frac{6.4}{0.116} = 55$$

With approximate values for the atomic weights of nitrogen and chromium, the relation between the exact relative combining weights and the exact atomic weights may be clarified.

2.5. Exact Relative Atomic Weights

From the study of three nitrogen-oxygen compounds there were obtained three values representing accurate relative combining weights of the element nitrogen, *i.e.*, 28.016, 14.008, and 7.004. Further, it is known that the approximate weight of the nitrogen atom is 14. Consequently, 14.008 must be the exact relative atomic weight of nitrogen, and the other two values for the combining weight of nitrogen should become equal to 14.008 when multiplied by the ratio of two small whole numbers.

$$28.016 \times \tfrac{1}{2} = 14.008$$

$$7.004 \times \tfrac{2}{1} = 14.008$$

Up to this point there may have existed a reasonable doubt as to the need for securing three different (but related) values for the combining weight of nitrogen. However, it should now be apparent that, if three such values all lead to the same value for the relative atomic weight of nitrogen (14.008), there should seem little reason to question the correctness of this value. In addition, the result obtained using one value for the combining weight serves as a check on the accuracy of other results.

If the approximate atomic weight of chromium is 55 and the values for the exact relative combining weights of chromium are 52.032, 34.688, and 17.344, then the exact relative atomic weight of chromium must be 52.032, since

$$52.032 \times \tfrac{1}{1} = 52.032$$

$$34.688 \times \tfrac{3}{2} = 52.032$$

$$17.344 \times \tfrac{3}{1} = 52.032$$

2.6. Review

The foregoing discussion is intended to show that the problem of assigning to each kind of atom a numerical value representing the relative weight of that atom involves the following steps:

1. The atom must be recognized as the smallest unit of matter that can participate in a chemical reaction.
2. A suitable standard must be established.
3. From experimental data showing the weights of the element combined with known weights of oxygen (or another element whose atomic weight relative to oxygen is already known), values for the relative combining weights are calculated.
4. By some suitable method, an experimental value for the approximate atomic weight of the element must be obtained.
5. With the approximate atomic weight and the exact relative combining weight known, the exact relative atomic weight is obtained by multiplying the combining weight by the ratio of two small whole numbers. The small whole numbers that make up this ratio are so chosen that the result is the number nearest to the approximate atomic-weight value.

With this summary in mind, it is suggested that the student re-study Secs. 2.1 to 2.5 before proceeding.

2.7. Meaning of Relative Atomic-weight Values

Since atoms are so small that they cannot be seen even with the aid of the most powerful microscope, the chemist cannot work with single atoms. Rather than work with a single atom of nitrogen, it is necessary to work with "bundles" of atoms, and of course the chemist chooses bundles of convenient size.

Although the exact values for the relative atomic weights of the elements, being arbitrary, may be expressed in any desired units (grams, pounds, tons, etc.), they are most frequently expressed in grams. Hence, the atomic weight of oxygen, 16, when expressed in grams, is referred to as the *gram-atomic weight of oxygen* or as *one gram atom of oxygen*. Similarly, 1.008 g. of hydrogen constitutes 1 gram-atomic weight or 1 gram atom of hydrogen. The atomic weight of an element, therefore, is merely the weight of an arbitrarily chosen quantity of that element. A list of the most accurate known values for the relative atomic weights of the elements is given on the inside front cover of this book.

Absolute Weights of Atoms. If the bundle of oxygen atoms in terms of which the chemist chooses to work has a weight of 16 g., the question naturally arises as to how many atoms are present in this particular size of bundle. Since atoms are so small, it would certainly be evident that in 16 g. of oxygen, for example, there must be an exceedingly large number of atoms. The actual number is known with

a fair degree of accuracy. As determined by a variety of methods which need not be discussed at this point, the number is believed to be 602,000,000,000,000,000,000,000,[1] or, expressed more conveniently, 6.02×10^{23}. This is known as *Avogadro's number*. Because the atomic weights of the other elements are expressed in relation to the atomic weight of oxygen, 1 gram-atomic weight of any element contains 6.02×10^{23} atoms of that element. Thus 1.008 g. of hydrogen must consist of 6.02×10^{23} atoms of hydrogen, and 23 g. (1 gram atom) of sodium must contain 6.02×10^{23} atoms of sodium. This remarkable result enables the chemist to work not only with a known weight of an element but, at the same time, a known number of atoms of that element.

If in 16 g. of oxygen there are 6.02×10^{23} atoms of oxygen, then the absolute weight of the single oxygen atom must be

$$\frac{16}{6.02 \times 10^{23}} = 0.000,000,000,000,000,000,000,026 \text{ g.} = 2.6 \times 10^{-23} \text{ g.}$$

Similarly, 1 gram-atomic weight of hydrogen (1.008 g.) contains 6.02×10^{23} atoms, each having the weight given by

$$\frac{1.008}{6.02 \times 10^{23}} = 0.000,000,000,000,000,000,000,001,67 \text{ g.} = 1.67 \times 10^{-24} \text{ g.}$$

Such numbers should convince even the most skeptical of the wisdom of using the *relative* rather than the *absolute* weights of atoms.

[1] This number, as well as some that follow, illustrates a problem not infrequently encountered in the study of chemistry. It is often necessary to deal with very large or very small numbers, and the task of representing such quantities can become very laborious and cumbersome. To avoid these difficulties, use is made of exponential expressions in which very large or very small numbers are represented in terms of exponents of the number 10. Thus, the number of atoms in a gram-atomic weight of any element is represented as 6.02×10^{23}, which means that the number 6.02 is to be multiplied 23 times by the number 10. If this is done, the result is 602,000,000,000,000,000,000,000. To use another example, the total weight of the atmosphere surrounding the earth has been estimated to be equal to 5,200,000,000,000,000,000,000 g. This number can be represented much more conveniently in exponential form as 5.2×10^{21}.

Small numbers also may be expressed conveniently by the use of negative exponents. Thus, the number 0.000,000,001 may be expressed as 1×10^{-9} since

$$0.000,000,001 = \frac{1}{1,000,000,000} = \frac{1}{10^9} = 1 \times 10^{-9}$$

Similarly, the number that represents the absolute weight of the individual oxygen atom is 0.000,000,000,000,000,000,000,026 g. In terms of negative exponents, this number becomes 26×10^{-24} or 2.6×10^{-23}.

2.8. Relative Weights of Molecules

Since molecules consist of atoms, it follows that the relative weight of a molecule (of an element or a compound) is simply the sum of the relative weights of the atoms in the particular molecule. If, for example, the molecule of the element oxygen contains 2 atoms, each having a relative weight of 16 units, then the weight of the oxygen molecule must be $2 \times 16 = 32$. Similarly, since the water molecule contains 2 atoms of hydrogen and 1 atom of oxygen, the relative weight of the molecule of water must be $(2 \times 1.008) + 16 = 18.016$.

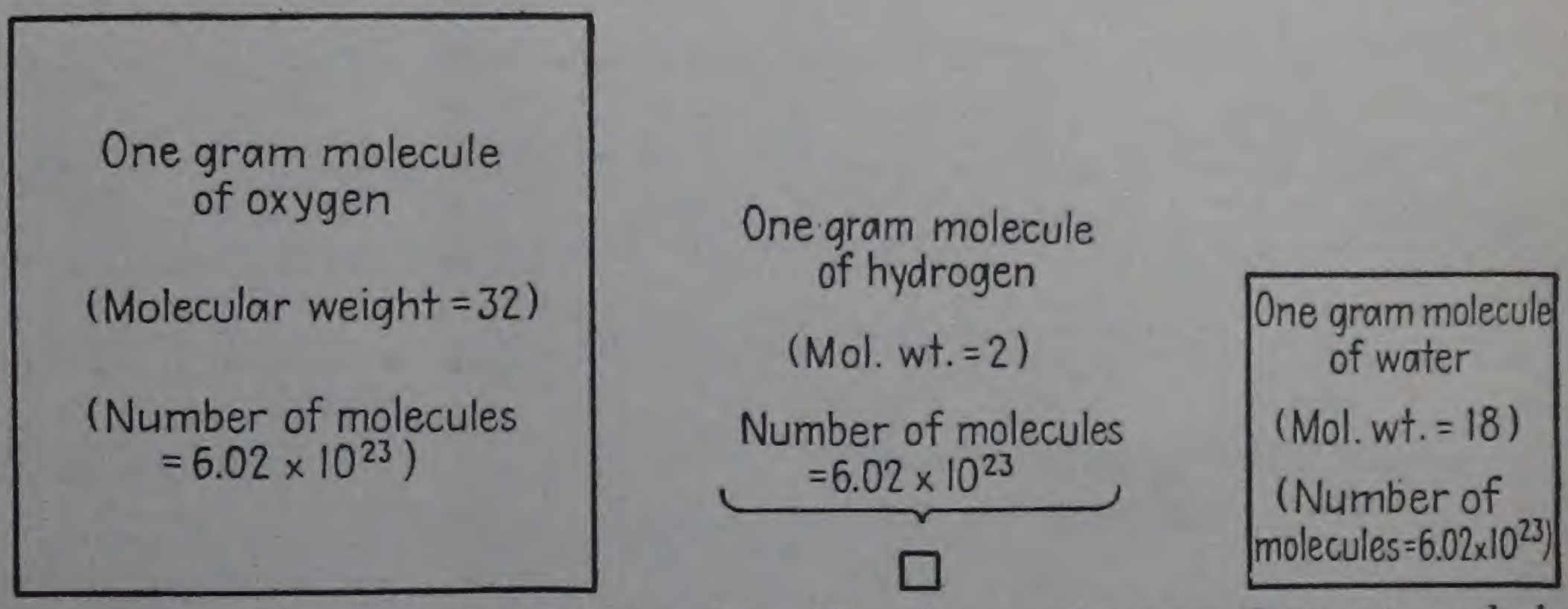
One gram molecule of oxygen
(Molecular weight = 32)
(Number of molecules = 6.02 x 10^23)
One gram molecule of hydrogen
(Mol. wt. = 2)
Number of molecules = 6.02 x 10^23
One gram molecule of water
(Mol. wt. = 18)
(Number of molecules = 6.02 x 10^23)

FIG. 7. Relative weights of molecules. The three squares are drawn to scale in proportion to the relative weights of the oxygen, hydrogen, and water molecules. Note particularly that the number of molecules in 1 gram-molecular weight is the same in all three cases regardless of the marked differences in the gram-molecular weights.

When expressed in grams, the weight of a molecule is referred to as either (*a*) 1 gram-molecular weight, (*b*) 1 gram molecule, or (*c*) 1 "mole." Thus, 32 g. of oxygen may be referred to by any of these designations. The number of *molecules* in 1 gram-molecular weight of any substance is the same as the number of *atoms* in 1 gram-atomic weight of an element, *i.e.*, 6.02×10^{23}. In 32 g. of oxygen there are 6.02×10^{23} molecules of the element oxygen; in 18.016 g. of water there are 6.02×10^{23} molecules of the compound water (Fig. 7).

GENERAL EXERCISES

1. What kinds of *experimental* data must one have in order to establish a value for the exact relative atomic weight of an element?
2. Define the following terms: (*a*) gram, (*b*) equivalent weight, (*c*) combining weight, (*d*) specific heat, (*e*) mole.
3. Explain clearly why 1 gram-molecular weight of water (which contains 16 g. of oxygen) must contain 6.02×10^{23} molecules of water.
4. Why is oxygen chosen as the standard for relative atomic weights, and why is the oxygen atom assigned a weight of 16.0000?

5. State, and illustrate, the law of multiple proportions.

6. How may one establish the relative atomic weight of an element if it does not form at least one compound with oxygen?

PROBLEMS[1]

1. From the analysis of a compound of sulfur it is found that the combining weight of sulfur is 8.015. The approximate atomic weight of sulfur is 31. Calculate the atomic weight of sulfur.

2. Calculations based on a knowledge of the percentage composition of a compound of chlorine and oxygen show that the combining weight of chlorine in this particular compound is 10.131. If the approximate atomic weight of chlorine is 35, calculate the atomic weight.

3. Carbon monoxide contains 57.15 per cent oxygen and 42.85 per cent carbon. Carbon dioxide contains 72.73 per cent oxygen and 27.27 per cent carbon. Calculate the combining weight of carbon in each of these compounds.

4. Aluminum oxide is a compound containing 52.91 per cent aluminum and 47.09 per cent oxygen. Calculate (*a*) the equivalent weight of aluminum in aluminum oxide, and (*b*) the combining weight of aluminum.

5. The approximate weight of the molecule of bromine is 162, and it is known that the bromine molecule contains 2 atoms. If the combining weight of bromine is 39.958, calculate the atomic weight.

6. An analysis of magnesium oxide shows that it consists of 60.31 per cent magnesium and 39.69 per cent oxygen. What is the combining weight of magnesium in this compound?

7. Three common oxides of iron have the following percentage composition: ferrous oxide, 77.73 per cent iron, 22.27 per cent oxygen; ferric oxide, 69.94 per cent iron, 30.06 per cent oxygen; ferrous-ferric oxide, 72.36 per cent iron, 27.64 per cent oxygen. For each of these compounds, calculate (*a*) the equivalent weight of iron, and (*b*) the combining weight of iron.

8. The specific heat of copper is 0.098 cal. What is the approximate atomic weight of copper?

9. Analysis of an oxide of copper shows that it consists of 20.11 per cent oxygen and 79.89 per cent copper. Calculate the combining weight of copper.

10. From the information obtained from Probs. 8 and 9, what is the atomic weight of copper?

11. If the specific heat of chromium is 0.116 cal. and the combining weight of chromium in chromium trioxide is 17.344, calculate (*a*) the approximate atomic weight of chromium, and (*b*) the atomic weight of chromium.

12. The specific heat of magnesium is 0.245 cal., and a value for the combining weight of magnesium is 12.16. What is (*a*) the approximate atomic weight, and (*b*) the atomic weight of magnesium?

13. An analysis shows that in one of its compounds, 8.99 g. of aluminum is combined with 16 g. of oxygen. If the specific heat of aluminum is 0.220 cal., what is the atomic weight of aluminum?

14. The specific heat of a certain element is 0.053 cal. Analysis of the oxide of this element shows that 1.7305 g. is combined with 0.4800 g. of oxygen. (*a*) What is the atomic weight of the element? (*b*) What is the symbol for the element in question?

[1] Numerical answers to problems are given in the back of the book.

15. A compound of carbon and sulfur was found to contain 8.8311 g. of sulfur in combination with 1.6538 g. of carbon. (*a*) Calculate the combining weight of sulfur in this compound. (*b*) If the sulfur atom is known to be approximately twice as heavy as the oxygen atom, what is the atomic weight of sulfur?

16. A compound of iron and chlorine contains 34.43 per cent iron and 65.57 per cent chlorine. (*a*) Calculate the combining weight of chlorine in this compound. (*b*) If the chlorine molecule contains 2 atoms and if the approximate molecular weight of chlorine is 70, what is the atomic weight of this element?

17. A certain compound formed by the elements iron and phosphorus contains 15.60 per cent phosphorus and 84.40 per cent iron. (*a*) What is the combining weight of phosphorus in this compound? (*b*) What is the atomic weight of phosphorus?

18. Express each of the following quantities in terms of *pounds:* (*a*) 200 g., (*b*) 1 kg., (*c*) 5 g.

19. Express each of the following quantities in terms of *grams:* (*a*) 2.8 lb., (*b*) 100 lb., (*c*) 1 oz.

20. Write the following numbers in exponential form: (*a*) 100,000, (*b*) 10,000,000,000, (*c*) 830,000,000, (*d*) 6,246,000, (*e*) 0.001, (*f*) 0.000,003,039, (*g*) 0.000,088,000, (*h*) 0.001,632.

21. Write the following numbers in the form of decimal fractions: (*a*) 1×10^{-10}, (*b*) 4.8×10^{-1}, (*c*) 6.748×10^{-6}, (*d*) 83×10^{-4}.

22. The atomic weight of lead is 207.21. Calculate the absolute weight of the lead atom.

23. From the information obtained in Prob. 10, calculate the absolute weight of the copper atom and express the result in both exponential and decimal form.

SUGGESTED READING

Journal of Chemical Education

Oesper, Some Famous Balances, **17**, 312 (1940).

Noyes, Standards of Length, Weight, and Volume in the United States, **5**, 586 (1928).

Rose, How Small Is a Molecule?, **6**, 1797 (1929).

Day and Sutton, The Combining Weight of Copper, **5**, 223 (1928).

Brescia and Rosenthal, The Atomic Weight of Hydrogen, **16**, 494 (1939).

Johnston, The Avogadro Number, **16**, 333 (1939).

Sunier, Some Methods of Determining Avogadro's Number, **6**, 299 (1929).

McAlpine, Percentage Composition and the Atomic Theory, **23**, 227 (1946).

Ellis and Linner, Determination of Exact Atomic Weights from Combining Weights, **26**, 528 (1949).

Kirkwood, A View of the Molecular World, **22**, 462 (1945).

CHAPTER 3

SYMBOLS, FORMULAS, EQUATIONS; CHEMICAL CALCULATIONS

The study and the practice of chemistry require frequent reference to a wide variety of chemical substances and chemical changes. The practice of referring to elements and compounds by name and that of providing detailed written descriptions of chemical changes would be exceedingly cumbersome. As a means of providing a more concise system of representation, chemists have developed what may be described as a system of "chemical shorthand." It is essential that the student of chemistry become thoroughly familiar with these methods of representation, since they are used throughout the beginning course and all subsequent courses in or experience with the subject.

FIG. 8. Jöns Jakob Berzelius (1779–1848). (*Courtesy of The Edgar Fahs Smith Memorial Collection in the History of Chemistry, The University of Pennsylvania.*)

3.1. Symbols

The method now used to represent the atoms of the elements was introduced by the Swedish chemist Berzelius (Fig. 8) in 1813. The symbols used are derived from the names of the elements by taking the initial letter, the first two letters, or other letters of the English or Latin names. Examples of the use of initial letters of English names are found in the symbols H (hydrogen), O (oxygen), C (carbon), etc. The symbol K for the element potassium was taken from the Latin name *kalium*. The symbol Ca is used for the element calcium since the initial letter has already been adopted as the symbol for carbon. Similarly Na (from the Latin

natrium) is used as the symbol for sodium. The symbol for the element magnesium consists of the first and third letters, Mg. There is given below a list of symbols for the common metals and nonmetals. These symbols are used repeatedly and should be made a part of the student's vocabulary.

TABLE 3
SYMBOLS FOR COMMON ELEMENTS

Metals		Nonmetals	
Name	Symbol	Name	Symbol
Aluminum	Al	Boron	B
Bismuth	Bi	Bromine	Br
Cadmium	Cd	Carbon	C
Calcium	Ca	Chlorine	Cl
Copper (*cuprum*)	Cu	Fluorine	F
Iron (*ferrum*)	Fe	Hydrogen	H
Lead (*plumbum*)	Pb	Iodine	I
Magnesium	Mg	Nitrogen	N
Manganese	Mn	Oxygen	O
Mercury (*hydrargyrum*)	Hg	Phosphorus	P
Potassium (*kalium*)	K	Silicon	Si
Silver (*argentum*)	Ag	Sulfur	S
Sodium (*natrium*)	Na		
Tin (*stannum*)	Sn		
Zinc	Zn		

Meaning of Symbols. The symbols for the elements are not merely abbreviations. In addition to showing the identity of an element, a symbol represents a definite weight of that element and consequently a definite number of atoms. The symbol H represents 1.008 parts by weight (grams) of hydrogen and, therefore, 6.02×10^{23} atoms of hydrogen. Similarly, the symbol K represents 39.1 parts by weight (grams) of potassium (6.02×10^{23} atoms). Since in scientific work weight is usually expressed in grams, the student should acquire the habit of thinking of the symbol for an element as representing 1 gram-atomic weight of that element. For example, each time the symbol O is encountered, it should be interpreted as representing 1 gram atom (16 g.) of the element oxygen.

3.2. Formulas

Just as symbols are used to represent atoms, formulas are used to represent molecules. The molecules so represented may be either ele-

mental or compound. The element oxygen exists, under ordinary conditions, in the form of molecules containing 2 atoms, and this may be shown by writing the symbol for oxygen and appending a subscript written to the right of the symbol, thus, O_2. Similarly, other elemental molecules are represented by formulas H_2, Cl_2, Br_2, etc.

Molecules of compounds are represented by writing side by side the symbols for the atoms that make up the molecules of the compound. Thus, hydrogen chloride is represented by the formula HCl. In the formulas for compounds containing hydrogen or a metal in combination with a nonmetal, the symbol for the nonmetal is usually (but not always) written last in the formula. If the number of one or more kinds of atoms in a given compound is greater than one, this fact must be shown by the formula. Therefore water, which is composed of 2 atoms of hydrogen and 1 atom of oxygen, has the formula H_2O. The formula H_2SO_4 shows that the hydrogen sulfate molecule is composed of 2 atoms of hydrogen, 1 atom of sulfur, and 4 atoms of oxygen. A subscript in a formula refers only to the symbol immediately preceding the subscript, unless placed outside of parentheses. Thus, in the formula for calcium hydroxide, $Ca(OH)_2$, the subscript applies to both the oxygen and the hydrogen.

Meaning of Formulas. Until the student acquires sufficient information to permit a distinction between kinds of chemical union, it is permissible to look upon all formulas as representing molecules. Since formulas are merely collections of symbols that have definite weight significance, it follows that a formula represents not only composition but also a definite weight of the substance concerned. The formula H_2 represents 2.016 (*i.e.*, 2×1.008) parts by weight of hydrogen, and the formula HCl represents 36.465 (*i.e.*, $1.008 + 35.457$) parts by weight of hydrogen chloride. Expressed in grams, these weights are called *gram-molecular weights* (gram molecules, or moles) of hydrogen and hydrogen chloride, respectively. The formula for potassium chlorate, $KClO_3$, shows that the molecule consists of 1 atom of potassium, 1 atom of chlorine, and 3 atoms of oxygen and represents 1 gram-molecular weight, 122.557 g. [*i.e.*, $39.1 + 35.457 + (3 \times 16)$], of potassium chlorate. From this example, it is seen that the (relative) weight of a molecule is simply the sum of the (relative) weights of all the atoms in that molecule.

3.3. Equations

The value of symbols and formulas with their attendant weight significance becomes most apparent in the representation of chemical

reactions. Consider the following statement: "Two hundred seven and twenty-one one-hundredths grams of the element lead unite with thirty-two grams of the element sulfur to form two hundred thirty-nine and twenty-one one-hundredths grams of the compound lead sulfide." Expressed in the language of symbols and formulas, this rather cumbersome description of a simple chemical reaction becomes

$$Pb + S = PbS$$

Since the total weight of matter represented to the left of the equality sign (207.21 g. + 32 g.) is equal to the total weight represented to the right (239.21 g.), the above expression may be called an *equation*. To indicate the direction of the chemical change, the equality sign is usually replaced by an arrow, which should be interpreted as indicating an equality, thus,

$$Pb + S \rightarrow PbS$$

The foregoing equation is a very simple one and may be written without difficulty. Suppose, however, that it is desired to write an equation representing the formation of water by the union of hydrogen and oxygen. First, there are written the symbols and formulas involved.

$$H + O \rightarrow H_2O \qquad (1)$$

Next, it must be recognized that hydrogen and oxygen exist not as atoms but rather in the form of elemental molecules. Hence the symbols must be replaced by the corresponding formulas.

$$H_2 + O_2 \rightarrow H_2O \qquad (2)$$

Expression (2), however, does not represent a true equality since on the left of the arrow (equality sign) there is shown a total of 2 atoms of oxygen while only 1 atom is shown on the right. Consequently the expression must be adjusted or balanced by the insertion of suitable coefficients,

$$2H_2 + O_2 \rightarrow 2H_2O \qquad (3)$$

leading to a true equality or equation. The overscoring of the symbols or formulas for gases represented in chemical equations is a common practice, but one not followed consistently. (In the remainder of this book, symbols or formulas for reactants or products that are gases are overscored only where it is desired to emphasize the physical state of the substance in question.)

Equation (3) should be read as follows: "Two moles of hydrogen ($2 \times 2.016 = 4.032$ g.) combine with 1 mole of oxygen (32 g.) to form 2 moles ($2 \times 18.016 = 36.032$ g.) of water."

Steps Involved in Writing Equations. From the foregoing example, it appears that the writing of a chemical equation involves the following steps:

1. Write to the left of the arrow the correct symbols or formulas for the substances that undergo change.
2. To the right of the arrow write the correct symbols or formulas for the products of the reaction.
3. Adjust or balance the expression so that a true equality results.

The application of this process may be illustrated by considering the equation representing the decomposition of potassium chlorate. It is necessary first to know (as the result of suitable experiments) that, when potassium chlorate is heated, it decomposes into potassium chloride and oxygen. With this information, the formula for the substance which undergoes change and the formulas for the products may be written (steps 1 and 2),

$$KClO_3 \rightarrow KCl + O_2$$

In order that the total number of atoms of oxygen involved may be such that all of the oxygen can be represented as diatomic molecules, it is necessary to insert the coefficient 2 before the formula for potassium chlorate.

$$2KClO_3 \rightarrow KCl + O_2$$

In the balancing of this expression, however, one must recognize the fact that the coefficient inserted modifies all that follows in the formula. Thus, $2KClO_3$ represents a total of 2 atoms of potassium, 2 of chlorine, and 6 (*i.e.*, 2×3) of oxygen. This same total number of atoms must also be represented on the right of the arrow.

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

The resulting expression is a true equation.

Information Provided by Equations. A correctly written chemical equation embodies the following items of information:

1. The identity of each of the substances (commonly known as the *reactants*) that take part in the reaction.
2. The identity of each of the products of the reaction.
3. The weight relationships between the reactants and the products.

Information Not Provided by Equations. Although chemical equations are extremely useful as a convenient means of describing chemical reactions, there are several important items of information that ordinarily cannot be incorporated in equations:

1. An equation gives little or no information concerning the properties of the reactants and products.
2. The fact that a particular chemical equation is written does not mean that the reaction represented will actually occur at all.
3. An equation usually provides no information as to the experimental conditions required for the successful completion of the reaction indicated.
4. An equation provides no indication as to the extent to which a given reaction will proceed in the direction suggested by the arrow.

Although these limitations may at first glance appear to be serious, several means of overcoming certain of these deficiencies become apparent as the student becomes more familiar with equations and their use.

CHEMICAL CALCULATIONS

In the preceding chapter it was shown that the study of weight relationships led to the establishment of certain fundamentally important laws and to values for the exact relative atomic weights of the elements. This information, together with a knowledge of the nature of symbols, formulas, and equations, leads to the question as to how these relationships may be used in solving problems of a practical character.

3.4. Establishment of Formulas

The formulas for chemical substances are established as the result of experiment. Two kinds of formulas are considered here: (1) the simplest formula and (2) the true formula. In either case, the initial experimental information required is a knowledge of the percentage composition of the compound in question, or experimental data from which the percentage composition may be calculated.

Simplest Formula. Suppose that a quantitative chemical analysis of a compound shows that it consists of 44.89 per cent potassium, 18.37 per cent sulfur, and 36.74 per cent oxygen. In 100 parts by weight of this compound, there are 44.89 parts by weight of potassium, 18.37 parts by weight of sulfur, and 36.74 parts by weight of oxygen. If these relative proportions by weight are divided by the respective atomic weights, the resulting quotients are the number of gram atoms of each of the three elements in 100 parts by weight of the compound.

$$\frac{44.89}{39.1} = 1.15 \text{ gram atoms of K}$$

$$\frac{18.37}{32} = 0.57 \text{ gram atom of S}$$

$$\frac{36.74}{16} = 2.29 \text{ gram atoms of O}$$

From this result it might appear that the formula for the compound is $K_{1.15}S_{0.57}O_{2.29}$. These fractional subscripts may not be used, however, since only whole numbers of atoms unite to form compounds. If the fractional subscripts may not be used as such, they at least express the correct ratio between the three kinds of atoms. The whole-number ratio is obtained by dividing each of the fractional subscripts by the smallest one,

$$\text{K:} \quad \frac{1.15}{0.57} = 2.02$$

$$\text{S:} \quad \frac{0.57}{0.57} = 1.00$$

$$\text{O:} \quad \frac{2.29}{0.57} = 4.02$$

from which it appears that the simplest formula for the compound must be K_2SO_4. The fact that the foregoing quotients do not turn out to be exactly whole numbers is attributable to experimental errors involved in determining the percentage composition of the compound.

In another case, the percentage composition of a compound is found to be 74.06 per cent oxygen and 25.94 per cent nitrogen. Just as before, one calculates the number of gram atoms of each kind of element,

$$\frac{74.06}{16} = 4.63 \text{ gram atoms of O}$$

$$\frac{25.94}{14.008} = 1.85 \text{ gram atoms of N}$$

and by dividing each of the resulting numbers by the smaller of the two, one reaches the conclusion that the compound contains 1.00 atom of nitrogen and 2.50 atoms of oxygen. The necessary whole-number ratio may obviously be achieved most simply by multiplying both of these numbers by 2, and this leads to the correct simplest formula, N_2O_5.

True Formula. In the illustrations already used, the simplest formulas also happen to be the true formulas for the compounds in

question. Accordingly, another example is used to illustrate the derivation of a simplest formula that differs from the true formula.

The analysis of a compound of mercury and chlorine shows that the compound consists of 85.11 per cent mercury and 14.89 per cent chlorine. As in the preceding examples, the relative numbers of atoms of mercury and chlorine present are

$$\text{Hg:}\quad \frac{85.11}{200.61} = 0.424; \qquad \frac{0.424}{0.419} = 1.01$$

$$\text{Cl:}\quad \frac{14.89}{35.457} = 0.419; \qquad \frac{0.419}{0.419} = 1.00$$

1 atom of mercury and 1 atom of chlorine. The simplest formula for the compound, therefore, is HgCl.

The question as to whether the simplest formula is the same as the true formula can be answered by a knowledge of the molecular weight of the compound. The weight of the molecule represented by the formula HgCl is 200.61 + 35.457 = 236.067. An experimental determination of the molecular weight of this compound, however, would show that the molecular weight is approximately 470. Since 470 is nearly twice 236.067, it follows that in each molecule of the compound there must be 2 atoms of mercury and 2 of chlorine. Accordingly, the true formula is Hg_2Cl_2.

3.5. Percentage Composition of Compounds

On many occasions the chemist wishes information concerning the percentage composition of pure chemical compounds. Of course, this information may be supplied by quantitative analysis of the substances concerned, but, *if the formula is known*, this same information may be had by a simple calculation. For example, the oxide of iron, Fe_2O_3, has a molecular weight of 159.68 [*i.e.*, the sum of the weights of all the atoms in the molecule: $(2 \times 55.84) + (3 \times 16) = 159.68$]. Hence,

$$\frac{(2 \times 55.84)}{159.68} \times 100\% = 69.94\%\ \text{Fe}$$

$$\frac{(3 \times 16)}{159.68} \times 100\% = 30.06\%\ \text{O}$$

Suppose that a chemist had available two compounds from which to produce zinc on a commercial scale, ZnS and $ZnCO_3$. All other factors being equal, it would seem desirable to use the compound containing

the greater percentage of zinc. This information may be obtained as follows:

$$\text{At. wt. of Zn} = 65.38$$
$$\text{Mol. wt. of ZnS} = 97.38$$
$$\text{Mol. wt. of } ZnCO_3 = 125.38$$
$$\text{Zn in ZnS} = \frac{65.38}{97.38} \times 100\% = 67.14\%$$
$$\text{Zn in } ZnCO_3 = \frac{65.38}{125.38} \times 100\% = 52.15\%$$

Other calculations may be made similarly (see the problems at end of chapter).

3.6. Calculations Based on Equations

No single type of chemical calculation is of more far-reaching importance than calculations related to equations. Such calculations serve many useful purposes. They serve as a basis for prediction, as a preliminary substitute for experiment, and as a check on the results of experiments.

If it is desired to produce hydrogen by the reaction between a metal and an acid, certain aspects of the problem may be clarified by a few simple calculations. On the assumption that tin and sulfuric acid are to be the reactants, the following equation may be written to represent the proposed reaction:

$$\underset{\text{(at. wt. = 118.7)}}{Sn} + \underset{\text{(mol. wt. = 98.016)}}{H_2SO_4} \rightarrow \underset{\text{(mol. wt. = 2.016)}}{\overline{H}_2} + \underset{\text{(mol. wt. = 214.7)}}{SnSO_4}$$

Calculation of Weight of Tin Required. Suppose the chemist wishes to produce exactly 25 g. of hydrogen and therefore would like to know how much tin would be necessary to produce this weight of hydrogen. The required information may be had by a simple calculation. The foregoing equation provides the information that 118.7 g. of tin is required to produce 2.016 g. of hydrogen. Now if this is true, then there must be some weight of tin which upon reaction with sulfuric acid will produce 25 g. of hydrogen. Whatever this unknown weight of tin may be, its relationship to 25 g. of hydrogen is the same as the relation between 118.7 g. of tin and 2.016 g. of hydrogen. If the unknown

weight of tin is represented by the traditional x, then these relationships may be expressed as a simple proportion in the following manner:

$$x:25::118.7:2.016$$

or

$$\frac{x}{25} = \frac{118.7}{2.016}$$

Solving for the value of x,

$$2.016x = 25 \times 118.7$$
$$x = \frac{25 \times 118.7}{2.016}$$
$$= 1472 \text{ g. Sn required}$$

From this result it appears that if 1472 g. of tin is allowed to react with sulfuric acid, there is produced 25 g. of hydrogen. The correctness of this result may be confirmed readily by experiment.

Calculation of Weight of Hydrogen Sulfate Required. Although it is required that there be present a quantity of hydrogen sulfate (as sulfuric acid) only sufficient (or more than sufficient) to react completely with the 1472 g. of tin, it might be of interest to know the exact weight of H_2SO_4 consumed in the production of 25 g. of hydrogen. This calculation may be made either on the basis of the weight of tin that reacts or on the basis of the weight of hydrogen formed. With y representing the unknown weight of H_2SO_4, this calculation is made on both bases:

On basis of Sn that reacts:

$$\frac{y}{1472} = \frac{98.016}{118.7}$$
$$118.7y = 98.016 \times 1472$$
$$y = \frac{98.016 \times 1472}{118.7}$$
$$= 1215 \text{ g. } H_2SO_4 \text{ required}$$

On basis of H_2 formed:

$$\frac{y}{25} = \frac{98.016}{2.016}$$
$$2.016y = 25 \times 98.016$$
$$y = \frac{25 \times 98.016}{2.016}$$
$$= 1215 \text{ g. } H_2SO_4 \text{ required}$$

Calculation of Weight of Stannous Sulfate Formed. Still another calculation based on this same equation may be made. By a similar calculation, the weight of stannous sulfate ($SnSO_4$) that is produced as a by-product of the formation of 25 g. of hydrogen may be found. In this case the calculation may be made in relation to (1) the weight of Sn that reacts, (2) the weight of H_2SO_4 that reacts, or (3) the weight of H_2 formed. That is, proportions may be represented in terms of any

one of the three factors known. With z representing the weight of $SnSO_4$, any one of the following three proportions may be used to secure the desired result:

(1)

$$\frac{z}{1472} = \frac{214.7}{118.7}$$

$$118.7z = 214.7 \times 1472$$

$$z = \frac{214.7 \times 1472}{118.7}$$

$$= 2662 \text{ g. } SnSO_4 \text{ formed}$$

(2)

$$\frac{z}{1215} = \frac{214.7}{98.016}$$

$$98.016z = 214.7 \times 1215$$

$$z = \frac{214.7 \times 1215}{98.016}$$

$$= 2662 \text{ g. } SnSO_4 \text{ formed}$$

(3)

$$\frac{z}{25} = \frac{214.7}{2.016}$$

$$2.016z = 25 \times 214.7$$

$$z = \frac{25 \times 214.7}{2.016}$$

$$= 2662 \text{ g. } SnSO_4 \text{ formed}$$

Of course, only one of these calculations need be made. The three are presented here only to show the relationship between the quantities of all of the substances involved.

Suggestion. In solving a problem the solution to which depends upon the quantitative relationships exhibited by chemical equations, it is suggested that the following procedure be adopted:

1. Write the correct equation representing the chemical reaction involved and the corresponding weight relationships.
2. Set up a proportion properly related to the equation.
3. Solve the proportion for the quantity sought.

For example, assume that it is necessary to know how much oxygen gas may be produced by the complete decomposition of 183 g. of potassium chlorate:

1. $$2KClO_3 \rightarrow 2KCl + 3O_2$$

2. $$2[39.1 + 35.457 + (3 \times 16)] = 245 \qquad 3(2 \times 16) = 96$$

$$\frac{x}{183} = \frac{96}{245}$$

3. $$245x = 96 \times 183$$

$$x = \frac{96 \times 183}{245}$$

$$= 71.7 \text{ g. } O_2 \text{ liberated}$$

Problems of this general type are encountered frequently, particularly in connection with laboratory work. Again it seems worth while to indicate that, although all the foregoing examples have been concerned with *grams* of various substances, the quantities involved could have been expressed just as readily in terms of other units, such as pounds or tons.

GENERAL EXERCISES

1. Distinguish clearly between the terms *symbol* and *formula*.
2. What fundamental law requires that the quantity of matter represented by the reactants in a chemical equation be equal to the quantity of matter represented by the products?
3. What information must one have in order to know whether the simplest formula for a compound is also the true formula?
4. In the formulas for chemical compounds, why must all of the subscripts be whole numbers?
5. Write equations for the reactions that occur when:

(*a*) The elements sulfur and oxygen combine to form a compound having the formula SO_3.

(*b*) This same product is formed by the reaction between the compound SO_2 and the element oxygen.

(*c*) The compound having the formula NH_3 decomposes to form the elements nitrogen and hydrogen.

(*d*) The elements aluminum and bromine unite to form the compound $AlBr_3$.

(*e*) The compound Fe_2O_3 reacts with hydrogen to form iron and water.

(*f*) The compound P_2O_5 reacts with water to form another compound having the formula H_3PO_4.

(*g*) The compounds $BaCl_2$ and H_2SO_4 react to form $BaSO_4$ and HCl.

(*h*) The element sodium reacts with water to form hydrogen and the compound NaOH.

PROBLEMS

1. What is the gram-molecular weight of each of the following compounds?

(*a*) MnO_2	(*b*) $Ca(OH)_2$	(*c*) KNO_3
(*d*) Al_2O_3	(*e*) $Na_2S_2O_3$	(*f*) $K_2Cr_2O_7$
(*g*) Na_2MnO_4	(*h*) $Zn_3(PO_4)_2$	(*i*) $HC_2H_3O_2$
(*j*) $Cu(H_2PO_4)_2$	(*k*) $Bi(OH)_2Cl$	(*l*) $Fe_2(SO_4)_3$

2. If, in carrying out a chemical reaction, one wished to use exactly 10 moles of cane sugar (formula, $C_{12}H_{22}O_{11}$), what weight (*a*) in grams, and (*b*) in pounds, would be required?
3. What is the percentage composition of compounds (*a*), (*b*), (*c*), and (*d*) in Prob. 1?
4. Calculate the percentage of the middle element present in compounds (*e*), (*f*), (*g*), and (*h*) in Prob. 1.
5. What is the simplest formula of the compound which contains 92.61 per cent mercury and 7.39 per cent oxygen?
6. A compound of lead is found to contain 90.66 per cent lead and 9.34 per cent oxygen. What is the simplest formula of this compound?

7. A pure compound known to contain only the elements sodium, carbon, and oxygen, was found by analysis to contain 43.4 per cent sodium and 11.3 per cent carbon. What is the simplest formula of the compound?

8. The analysis of a pure compound shows that it consists of 80.0 per cent carbon and 20.0 per cent hydrogen. (*a*) What is the simplest formula for this compound? (*b*) If the molecular weight of the compound is approximately 30, what is the true formula?

9. What is (*a*) the simplest formula and (*b*) the true formula of the compound which has a molecular weight of approximately 250 and which contains 79.8 per cent chlorine and 20.2 per cent aluminum?

10. A compound of carbon, hydrogen, and oxygen was found to have a molecular weight of approximately 138. By analysis, this compound was found to contain 52.2 per cent carbon and 13.1 per cent hydrogen. What is (*a*) the simplest formula, and (*b*) the true formula?

11. Calculate the weight of $KClO_3$ required for the production of 10 g. of KCl.

12. By the decomposition of some $KClO_3$ there was obtained 45 g. of oxygen. Calculate the weight of KCl that was also formed in this reaction.

13. Zinc reacts with hydrochloric acid (HCl) to form hydrogen gas and a compound having the formula $ZnCl_2$. What weight of HCl would be required to react with 10 g. of zinc?

14. The decomposition of mercuric oxide (HgO) by means of heat results in the formation of mercury and oxygen. (*a*) Calculate the weight of mercury (in tons) that will be produced by the decomposition of 7.56 tons of HgO. (*b*) Express the calculated result in terms of milligrams.

15. Silver nitrate and sodium chloride react in accordance with the equation: $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$. (*a*) What weight of AgCl is formed if a solution containing 150 g. of NaCl is added to a solution containing an excess of $AgNO_3$? (*b*) What weight of $NaNO_3$ is formed?

16. One method for the production of potassium chlorate involves the reaction: $3Cl_2 + 6KOH \rightarrow KClO_3 + 5KCl + 3H_2O$. (*a*) What weight of $KClO_3$ could be formed if one used 75 g. of KOH in this reaction? (*b*) What weight of KCl would be formed at the same time?

SUGGESTED READING

Journal of Chemical Education

Ewing, What's in a Name?, **15**, 123 (1938).
Hauben, The Derivation of the Names of the Elements, **10**, 227 (1933).
Jacobs, On the Writing of Chemical Equations, **15**, 75 (1938).
Simons, Chemical Equations, **3**, 1305 (1926).
Griffin, Calculation of Simplest Formula from Percentage Composition, **10**, 575 (1933).
Brautlecht, Computations in General Chemistry, **4**, 370 (1927).
Spicer, The Solution of Elementary Chemical Problems, **17**, 382 (1940).
Brinkley, Numerical Problems in General Chemistry, **4**, 1283 (1927).

CHAPTER 4

THE STRUCTURES OF ATOMS

In Chap. 1 all forms of matter were classified as consisting of elements, compounds, or mixtures, and it was further recognized that all of these various materials are composed of atoms. This leads naturally to inquiry into the nature of atoms and to a consideration of the kinds of particles of which atoms are composed. This kind of increasingly detailed study of the nature of the fundamental particles of matter reflects the scientist's desire to achieve a complete understanding of the nature of matter, and ultimately to have a better knowledge of the interrelationship of matter and energy. It is the purpose of the present discussion to present an elementary view of the nature of atoms and to make a beginning toward an understanding of how and why chemical reactions occur.

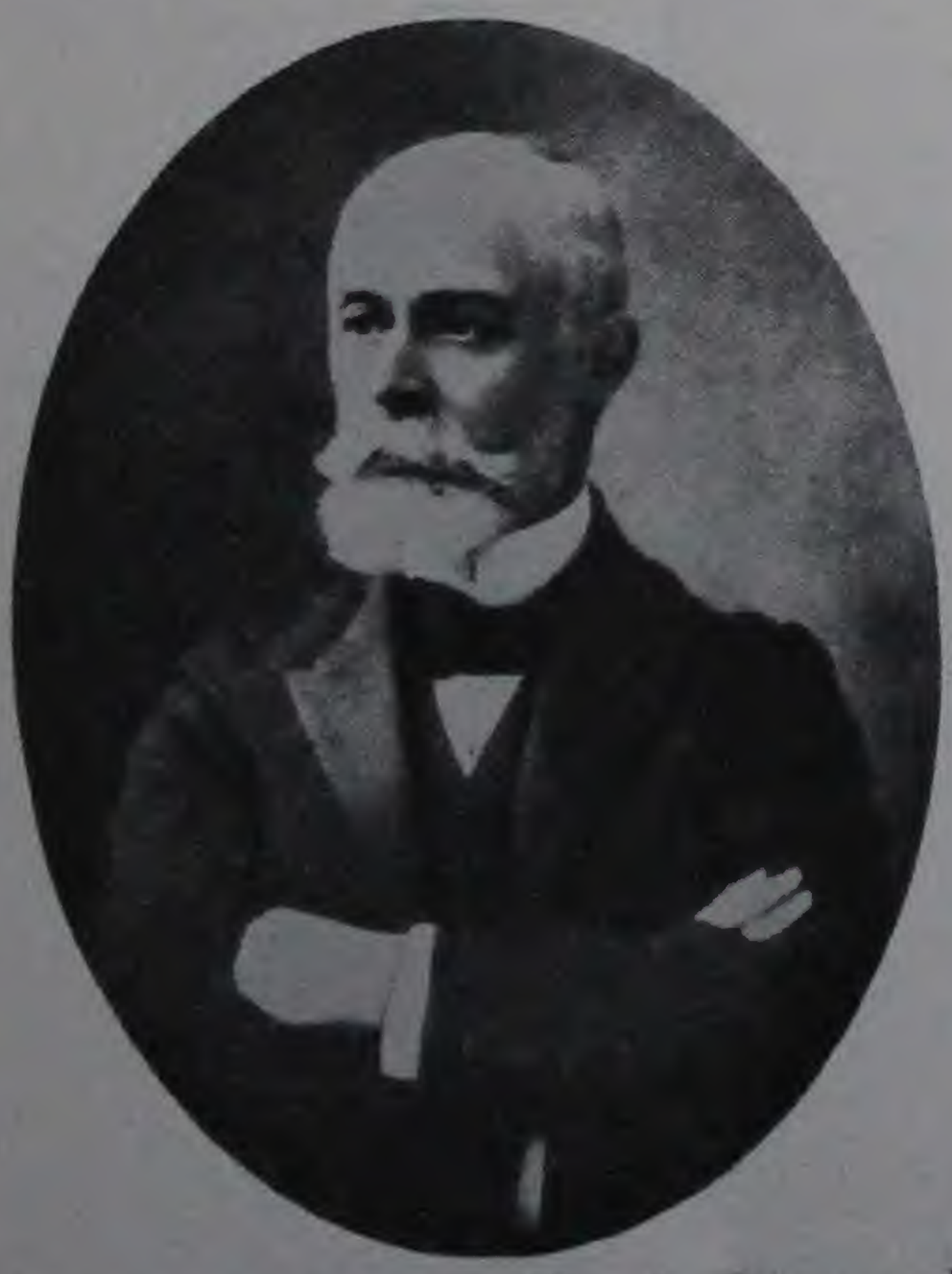

FIG. 9. Antoine Henri Becquerel (1852–1908). (*Courtesy of The Edgar Fahs Smith Memorial Collection in the History of Chemistry, The University of Pennsylvania.*)

4.1. Radioactivity

If one wishes to know what kinds of particles of matter are contained in atoms, it is helpful to know what kinds of particles can be obtained when these atoms are broken down (decomposed). It is fortunate that the atoms of some of the elements exhibit a type of behavior which makes it possible to acquire this kind of information.

Several of the elements of high atomic weight are unstable and undergo spontaneous disintegration. This property is known as *radioactivity* and was discovered by the French physicist Becquerel (Fig. 9) in 1896. Although the occurrence of radioactive change or

disintegration is not subject to control by man, much can be learned through the study of this somewhat unusual behavior. The progressive disintegration of radioactive elements such as uranium and radium produces a variety of lighter atoms having physical and chemical properties different from those of the parent radioactive elements. In addition, alpha particles, beta particles (or rays), and gamma rays are also produced. The properties of these particles or rays can be explained best in terms of an experiment illustrated by Fig. 10. If, for example, a sample of radium or a compound of radium is placed in a hole drilled into a block of lead (which serves as a shield), the particles and rays that are emitted during the radioactive disintegration of the radium atoms may be separated (deflected) by means of a magnet arranged at right angles to the path of the emitted particles and rays. If a photographic plate is placed in the path of the particles and the rays that have been separated by use of the magnet, each kind of particle or ray darkens the photographic plate at the point of impact. The properties of each of these products of radioactive change are considered separately in the following paragraphs.

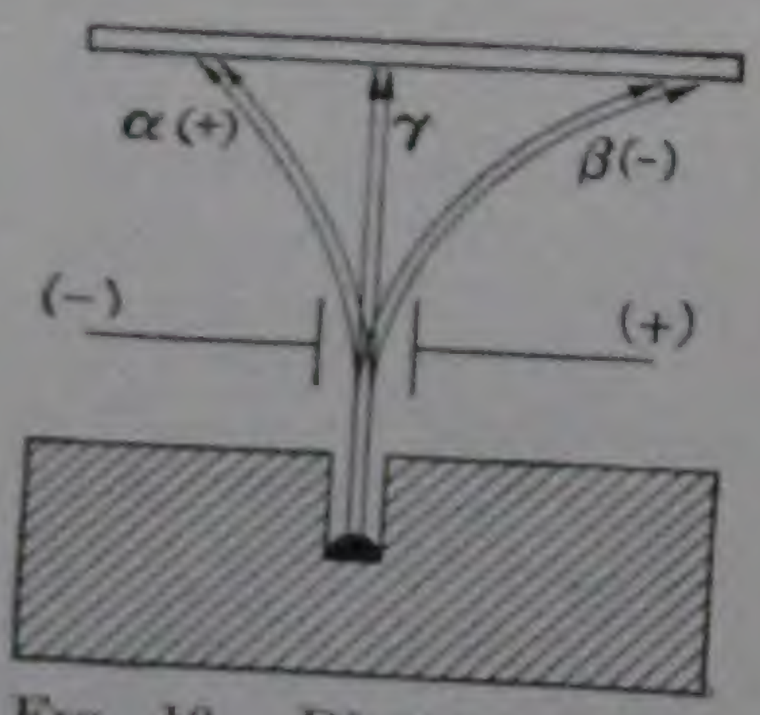

Fig. 10. Diagram representing deflection of alpha and beta particles by a magnetic field.

Alpha Particles. In their passage through the magnetic field, α-particles are deflected toward the negative pole of the magnet. An α-particle has a mass almost exactly the same as the mass of a helium atom but differs from the neutral helium atom in that the α-particle bears two unit charges of positive electricity. Although α-particles are emitted with velocities of the order of 10,000 miles per sec., they are not very penetrating since they are capable of passing through only extremely thin sheets (less than 0.1 mm. in thickness) of metals such as aluminum. α-Particles make only a relatively slight impression when they strike a photographic plate.

Beta Particles. As shown by Fig. 10, β-particles are deflected toward the positive pole of the magnet. These particles consist of unit particles of negative electricity, which are known as *electrons*. The β-particle has a mass only $\frac{1}{1845}$ that of the hydrogen atom and is emitted with a velocity of the order of 100,000 miles per sec. These β-particles (or electrons) are capable of penetrating thin sheets (1 mm. in thickness) of aluminum and are thus proved to be more penetrating than α-particles.

Gamma Rays. The γ-rays are not deflected by the magnetic field, and it may therefore be concluded that they bear neither positive nor negative electrical charge; hence they are said to be electrically neutral. These rays are similar to ordinary light waves except that γ-rays have extremely short wave lengths (Fig. 11). γ-Rays have essentially the same characteristics as X rays, which were discovered by the German physicist Röntgen, in 1895. That certain γ-rays are

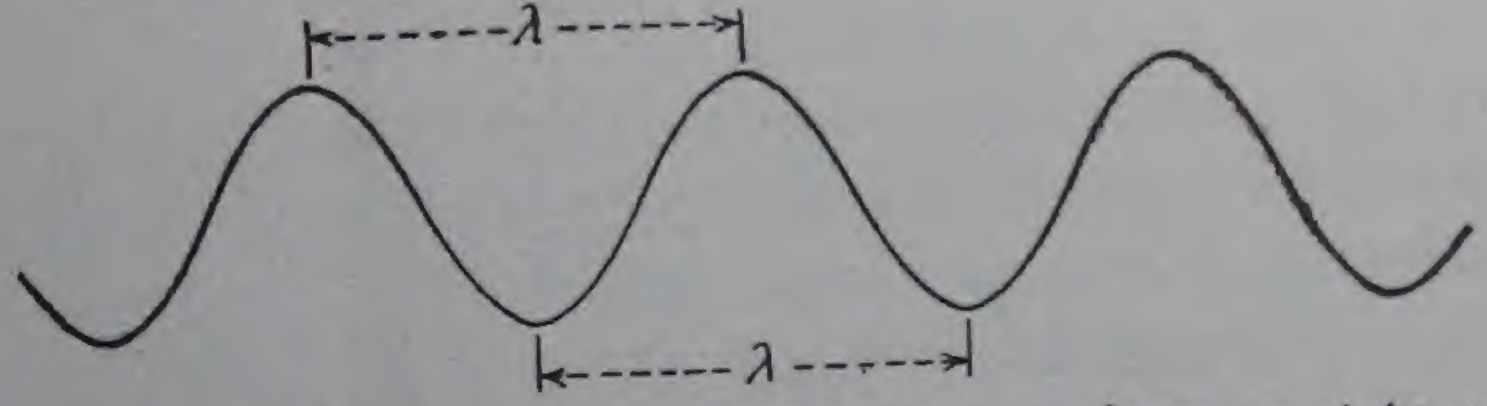

FIG. 11. Illustration of wave length. The distance from crest to crest or from trough to trough is called one wave length and is usually designated by the Greek letter *lambda* (λ).

extremely penetrating is shown by the fact that they may be detected (by means of a photographic plate) after having passed through a sheet of lead 10 in. thick.

4.2. Atomic Numbers

When an element is bombarded by a stream of electrons produced at the cathode of an X-ray tube (Fig. 12), the atoms of the element give off X rays. This procedure may be likened to the bombardment of a target by means of bullets. The element under investigation serves as the target, and the "bullets" consist of electrons impelled by relatively

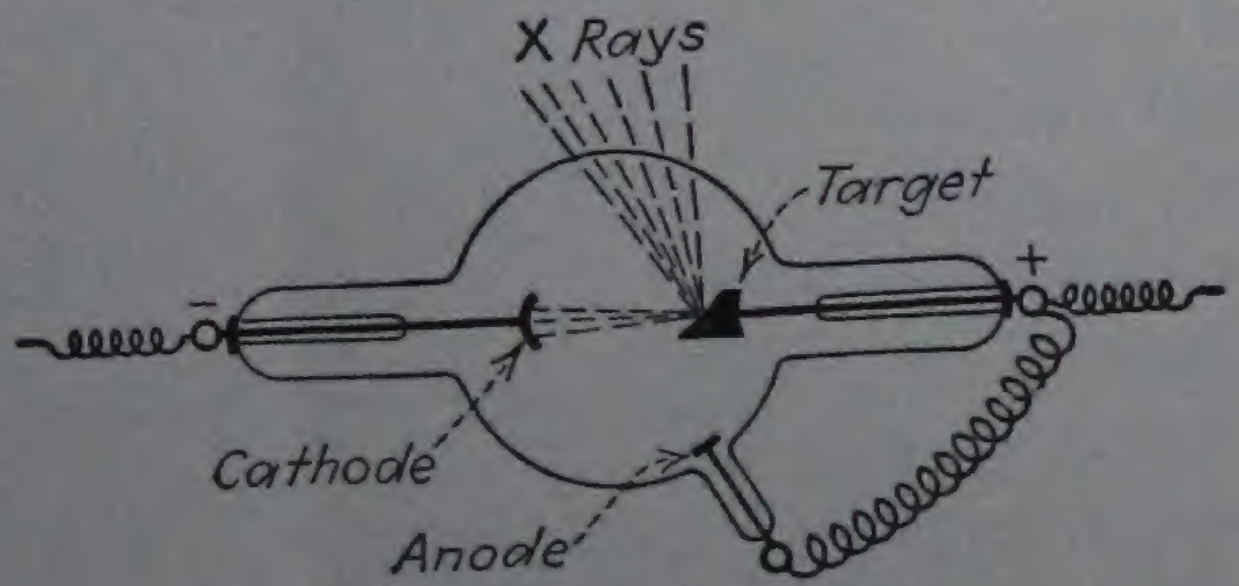

FIG. 12. An X-ray tube.

high voltages. Examination of the X-ray spectra of different elements has shown that each emits certain characteristic X radiations which are not found in the X-ray spectrum of any other element.

In 1913, the young English physicist Moseley (Fig. 13) announced a discovery of outstanding significance. As a result of the study of the X-ray spectra of many of the elements, Moseley found that, for any

two elements that stand next to each other in atomic weight, there is a constant difference between the square roots of the frequencies of vibration of the X rays characteristic of these two elements. (Frequency of vibration of X rays or light waves is the reciprocal of the wave length and is concerned with the number of "waves" produced as the wave describes its path through a certain distance such as 1 cm. Thus, the smaller the wave length, the greater is the frequency of vibration.) If the elements are arranged in a series based upon the order indicated by the frequencies of the characteristic X rays and if each element in this series is assigned a number beginning with the number 1 for hydrogen (the lightest known element), these assigned numbers are related to the frequency by the expression

FIG. 13. H. G. J. Moseley (1887–1915). (*Courtesy of The Edgar Fahs Smith Memorial Collection in the History of Chemistry, The University of Pennsylvania.*)

$$\sqrt{f} = k(N - a)$$

where f is the frequency of vibration, N is the assigned number, which is known as the *atomic number*, and k and a are constants. On this basis, the atomic number of hydrogen

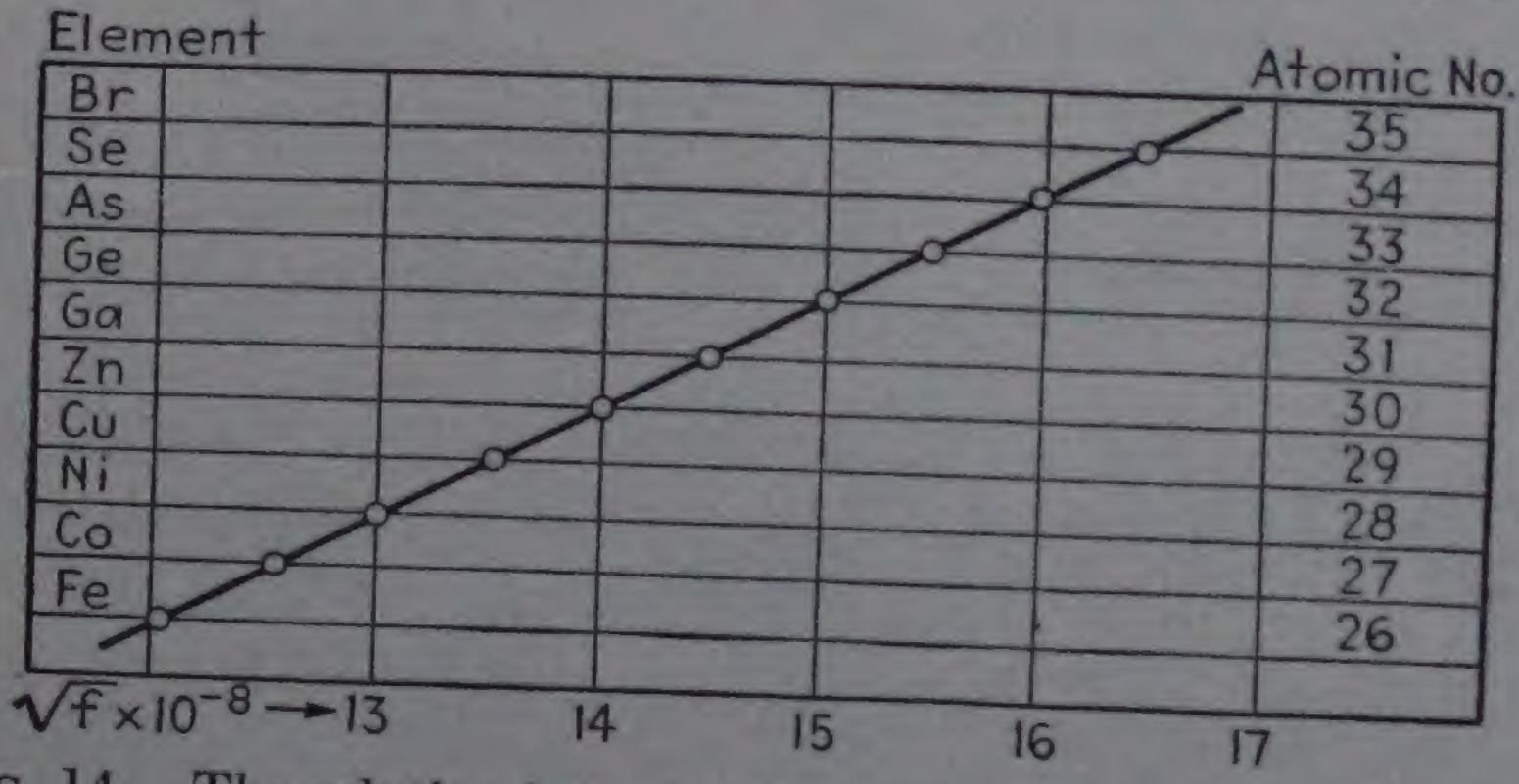

FIG. 14. The relation between frequency and atomic number.

is 1, that of helium is 2, that of lithium is 3, etc. The relation between frequency and atomic number for a few of the elements is shown in Fig. 14.

4.3. Components of Atoms

The property of radioactivity suggests that all atoms must be made up of units of matter much less complex than the simplest varieties of atoms. One of these particles, the electron, has already been seen to be emitted during the radioactive decay of the atoms of certain elements of high atomic weight. Two additional so-called *fundamental particles* must be considered before making any further inquiry into the internal make-up of atoms and molecules.

FIG. 15. E. Rutherford (1871–1937). (*Courtesy of The Edgar Fahs Smith Memorial Collection in the History of Chemistry, The University of Pennsylvania.*)

Proton. The existence of a unit negative particle of electricity (the electron) suggested that there must be a corresponding positive unit. Experiments performed by the English physicist Rutherford (Fig. 15) and others showed that, when certain light elements such as aluminum were bombarded by high-velocity α-particles, a new kind of particle was emitted from the atoms of the elements used as the target. Further study demonstrated that these particles bore a positive charge and that they were lighter than α-particles. These particles were named *prolons* and were found to have a mass almost identical with that of the hydrogen atom, or more precisely $^{1844}/_{1845}$ the mass of the hydrogen atom. The charge on the proton is equal to the charge of the electron but it is opposite in sign.

Neutron. By experiments similar to those which led to the discovery of the proton, the bombardment of several elements (particularly beryllium) by α-particles was shown to result in the emission of still another particle of matter known as the *neutron*. As is suggested by its name, this particle is electrically neutral (*i.e.*, it bears neither positive nor negative charge). On the scale of atomic weights based on O = 16.0000, the neutron has a mass identical with that of the hydrogen atom. The fact that the mass of the proton is $^{1844}/_{1845}$ that of the hydrogen atom plus the fact that the mass of the electron is

$\frac{1}{1845}$ that of the hydrogen atom suggests that the neutron consists of 1 proton and 1 electron.

Since electrons, protons, and neutrons are produced when different atoms are subjected to conditions so extreme as to cause decomposition to occur, it may be concluded that some or all of these particles of matter must be present in the atoms of all the elements. Despite the possibility that other particles (α-particles, for example) are involved, an adequate interpretation of the structures of atoms may for present purposes be made in terms of electrons, protons, and neutrons. The properties of these fundamental particles are summarized in Table 4.

TABLE 4
COMPONENTS OF ATOMS

Particle	Charge	Mass
Neutron	0	1.008
Electron	−	$\frac{1}{1845} \times 1.008$
Proton	+	$\frac{1844}{1845} \times 1.008$

4.4. Nature of Atoms

Knowledge gained from careful experimentation extending over many years has led to certain views with regard to the nature of the atoms of the various elements. These ideas may be summarized as follows:

1. An atom of any element is an electrically neutral body containing a central *nucleus*, the dimensions of which are small in comparison with the dimensions of the atom as a whole. This nucleus consists of protons and neutrons and represents practically the entire mass (weight) of the atom. The nucleus of the atom possesses an excess of positive charges (protons), and the magnitude of this charge is identical with the atomic number of the element.

2. The extranuclear structure (*i.e.*, that outside of the nucleus) consists of electrons which may be thought of as rotating in *orbits* about the central nucleus in a manner similar to the rotation of the planets about the sun. All the electrons in orbits that are approximately the same distance from the nucleus are said to be in the same *shell*. Since the normal atom is electrically neutral, the total number of these electrons must be the same as the positive charge on the nucleus, and hence the same as the atomic number of the element concerned. The shell

farthest removed from the nucleus may not contain more than 8 electrons.

Those properties of an atom which are dependent upon mass are related to the nucleus of the atom, while *the chemical properties are determined by the number and arrangement of electrons outside the nucleus.*

4.5. Diagrams Representing the Structures of Atoms

In terms of the foregoing ideas, it becomes desirable to attempt to represent the structures of atoms by suitable two-dimensional diagrams. Since atoms cannot be seen, it must be recognized that any static two-dimensional picture drawn to represent such dynamic three-dimensional objects may be very inaccurate. However, these diagrams are useful in the interpretation of chemical reactions and in gaining some ideas concerning the structures of molecules; hence, the use of these diagrams is justifiable.

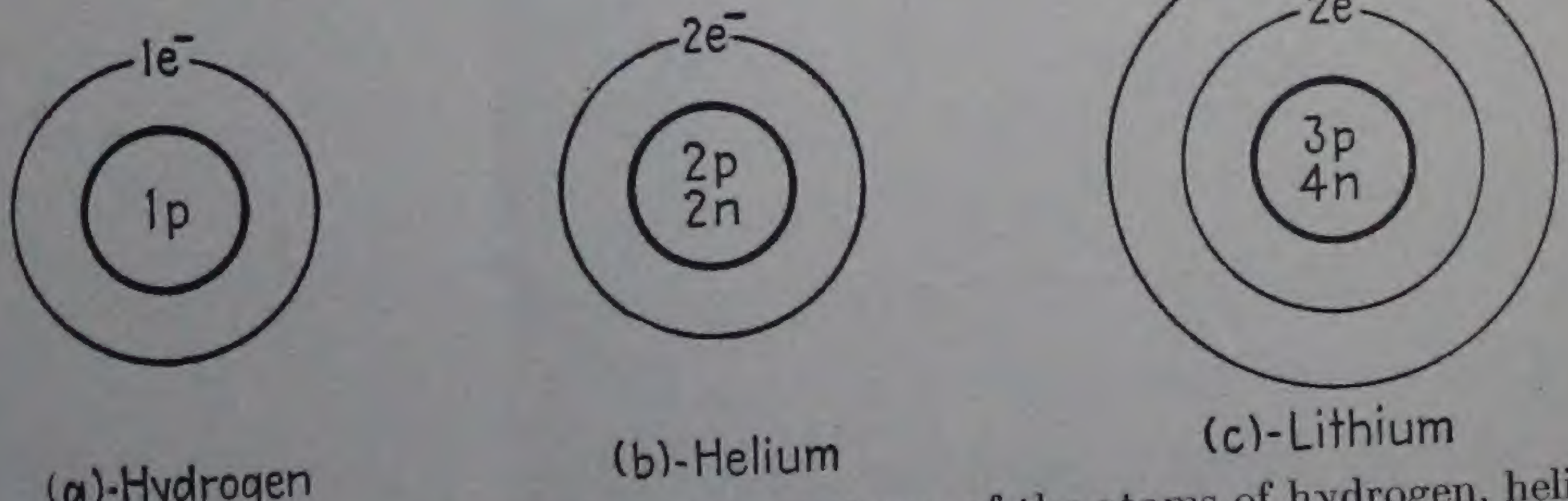

FIG. 16. Diagrams representing the structures of the atoms of hydrogen, helium, and lithium.

Hydrogen Atom. The atomic number of hydrogen is 1, and the nucleus of this atom therefore must contain 1 proton, which is indicated by the letter *p* in the small circle that represents the nucleus of the hydrogen atom (Fig. 16*a*). Since the atomic weight of hydrogen is essentially 1, this proton alone must make up the entire nucleus of the hydrogen atom. This is the only kind of atom containing no neutrons in the nucleus. Since the hydrogen atom is electrically neutral, the extranuclear structure must consist of 1 electron (represented by e^-), which may be pictured as rotating in an orbit outside of the nucleus. The hydrogen atom differs from all others in the simplicity of its structure. In order to gain a mental picture of the hydrogen atom, one need only visualize a single electron rotating around a nucleus consisting of a single proton.

Helium Atom. Since the atomic number of helium is 2, there must be 2 protons in the nucleus and 2 electrons outside of the nucleus.

However, 2 protons in the nucleus are insufficient in terms of mass to account for the fact that the atomic weight of helium is 4. Consequently, this nucleus must also contain 2 neutrons, and the structure of the helium atom may be represented by the diagram of Fig. 16*b*, where *n* represents a neutron. This diagram implies that the 2 electrons rotate in the same orbit, an implication that may be misleading. Actually, all that one wishes to represent by such a diagram is that these 2 electrons are in orbits in the same shell. Furthermore, since these electrons are in motion about the nucleus, there seems little to be gained by assigning to each a fixed position in the shell. With but few exceptions (Sec. 4.10), therefore, it is sufficient merely to indicate the total number of electrons in the shell, as shown in Fig. 16*b*.

Lithium Atom. That the nucleus of the lithium atom contains 3 protons follows from the atomic number of this element. However, the atomic weight of lithium is represented by the decimal fraction 6.9. For reasons that are given in Sec. 4.6., these fractional atomic weights may be rounded off to the nearest whole number for the purposes of the present discussion. Accordingly, the atomic weight of Li is considered to be 7, and there must be 4 neutrons in the nucleus of the lithium atom in addition to the 3 protons. The only additional complication that arises is concerned with the fact that the shell nearest the nucleus may not contain more than 2 electrons and, from its atomic number, the lithium atom is seen to have 3 electrons. The third electron must necessarily rotate in a shell farther removed from the nucleus, *i.e.*, in a second shell, as shown in Fig. 16*c*.

The case of lithium naturally raises the question as to the limitations on the number of electrons that may be represented as rotating in any given shell. This information is given in Table 5, where the shells are listed in increasing order of distance from the nucleus.

TABLE 5

MAXIMUM NUMBERS OF ELECTRONS IN THE VARIOUS SHELLS

Shell	Number of Electrons
First	2
Second	8
Third	18*
Fourth	32
Fifth	18
Sixth	8

* It must be kept in mind that the outermost shell may not contain more than 8 electrons. Thus, if a given atom involves only three shells, 8 (and not 18) is the maximum number of electrons in the third shell. In order for the third shell to contain more than 8 electrons, additional shells beyond the third are necessary.

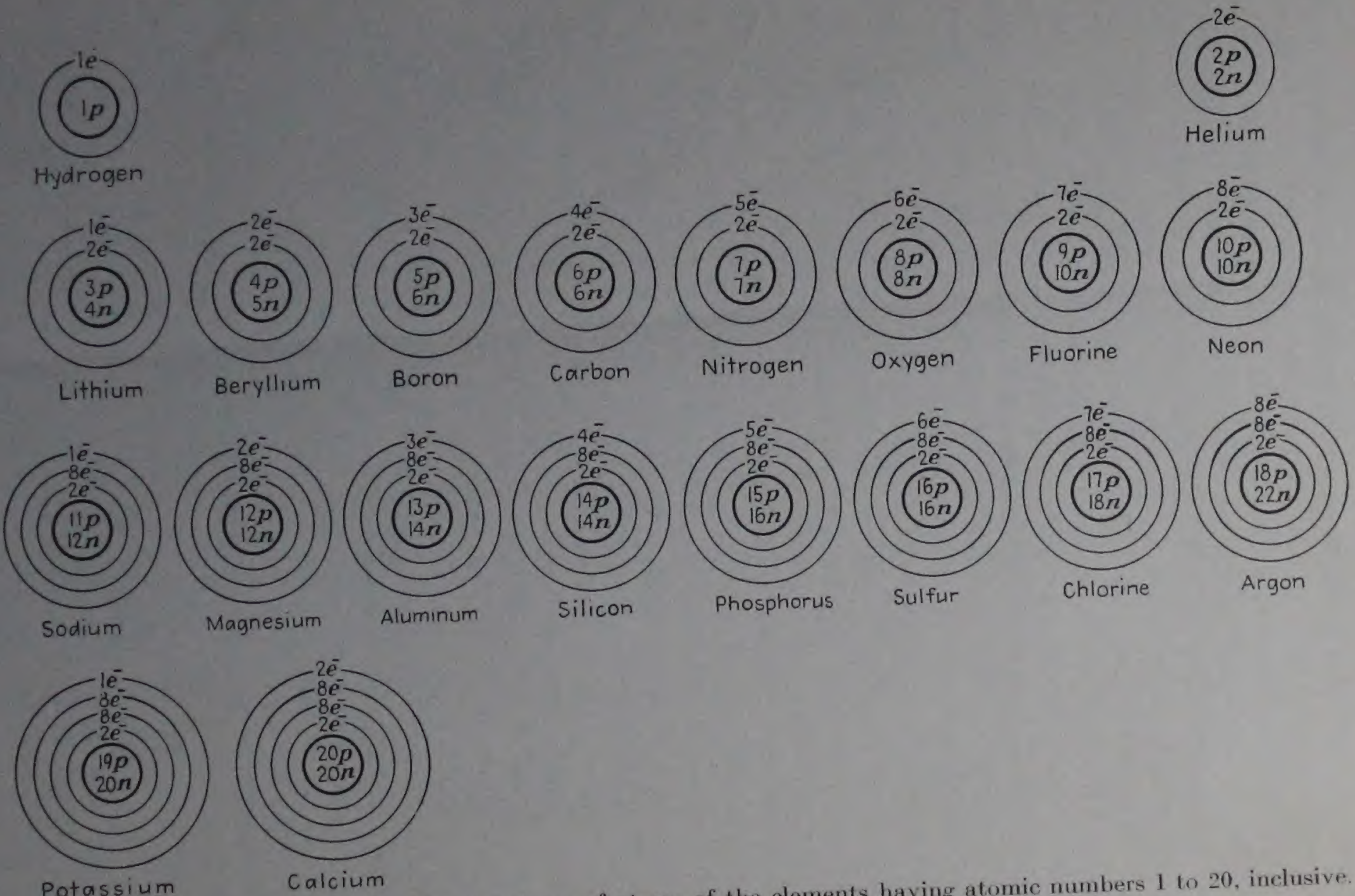

FIG. 17. Diagrams representing the structures of atoms of the elements having atomic numbers 1 to 20, inclusive.

Structures of Other Atoms. In the manner illustrated above, similar diagrams may be drawn to represent the structures of other kinds of atoms. Diagrams corresponding to atoms of the elements having atomic numbers 1 to 20 inclusive are assembled in Fig. 17; the particular manner in which these diagrams are arranged is worthy of further comment.

Emphasis has already been placed upon the fact that the *chemical properties* of the elements depend upon the number and arrangement of the extranuclear electrons in their atoms. Those elements consisting of atoms having the same number of electrons in the outermost shell might therefore be expected to exhibit at least some degree of chemical similarity. Such elements are indeed strikingly similar in their chemical properties, and it is for this reason that the diagrams which display this feature of structural similarity are arranged in vertical columns in Fig. 17. A more elaborate consideration of the manner in which elements may be classified in terms of the structures of their atoms is postponed to Chap. 16, *i.e.*, until after the student has acquired a greater familiarity with some of the chemical elements, their compounds, and the simple reactions of both.

4.6. Isotopes

For the purpose of drawing diagrams of the atoms of some of the elements, the atomic weights in certain cases were taken as the nearest whole numbers. It was once believed that the atomic weights of all the elements should be represented by whole numbers and that fractional atomic weights were due to errors in the determination of atomic weights. However, discoveries made by the English physicists J. J. Thomson and F. W. Aston demonstrated that the atoms of a given element are not necessarily all alike in mass. For example, the atomic weight of the element nitrogen as found by chemical methods is 14.008. However, nitrogen is known to exist in nature in the form of a mixture of nitrogen atoms of atomic weight equal to 14 and nitrogen atoms having an atomic weight of 15. These two are present in the naturally occurring mixture in a constant ratio such as to make the average atomic weight equal to 14.008. Since these two kinds of nitrogen atoms differ only with respect to weight, they differ only in the number of neutrons in the nucleus. The atomic numbers

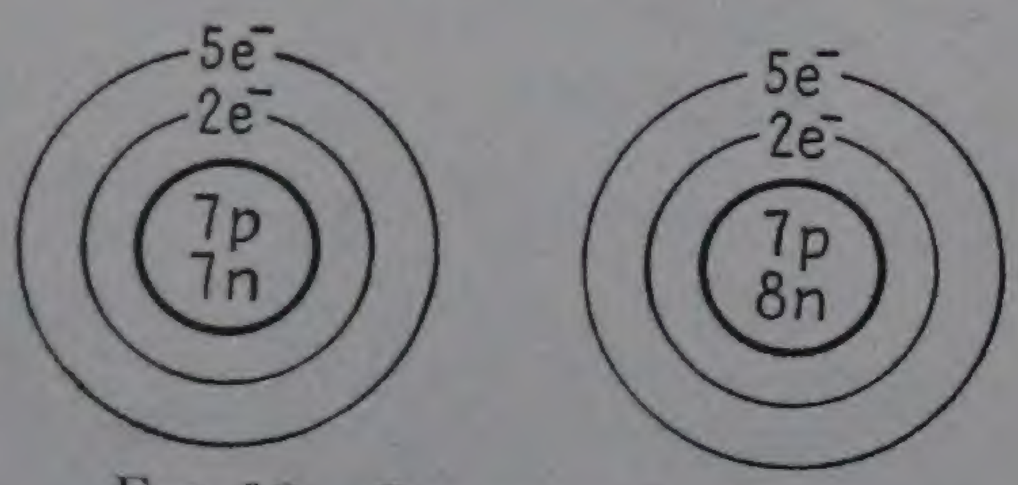

FIG. 18. Isotopes of nitrogen.

and the extranuclear structures must be the same; hence, the two are identical so far as their chemical properties are concerned. *Atoms having the same atomic number but different atomic weights are called isotopes.* Diagrams of the two isotopes of nitrogen are shown in Fig. 18. From the preceding discussion, it should not be inferred that the relative weights of isotopes are *exactly* whole numbers. For example, the weight of "chlorine 35" is actually 34.98054.

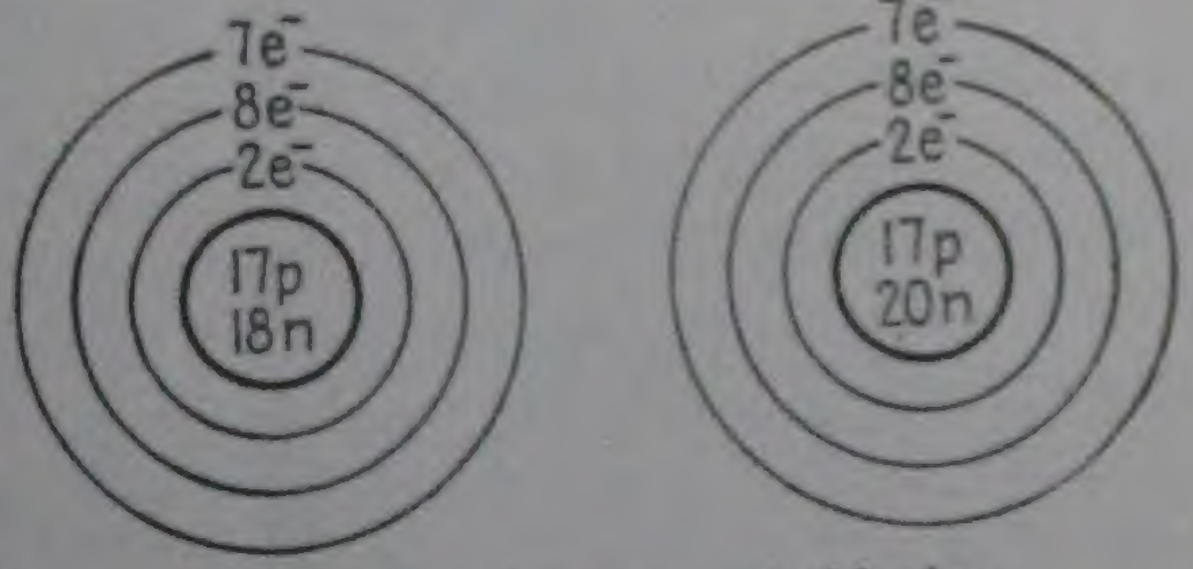

FIG. 19. Isotopes of chlorine.

Similarly, it has been shown that most of the elements consist of mixtures of isotopes. Chlorine consists of two isotopes (Fig. 19); calcium, 4; tin, 10; etc. A complete list of known stable isotopes of the elements is given in the Appendix. Inspection of this list reveals that, so far as is now known, only a few elements (Co, F, Al, P, As, etc.) consist entirely of atoms all of which are the same. Further, it is seen that some elements having whole-number atomic weights consist of mixtures of isotopes.

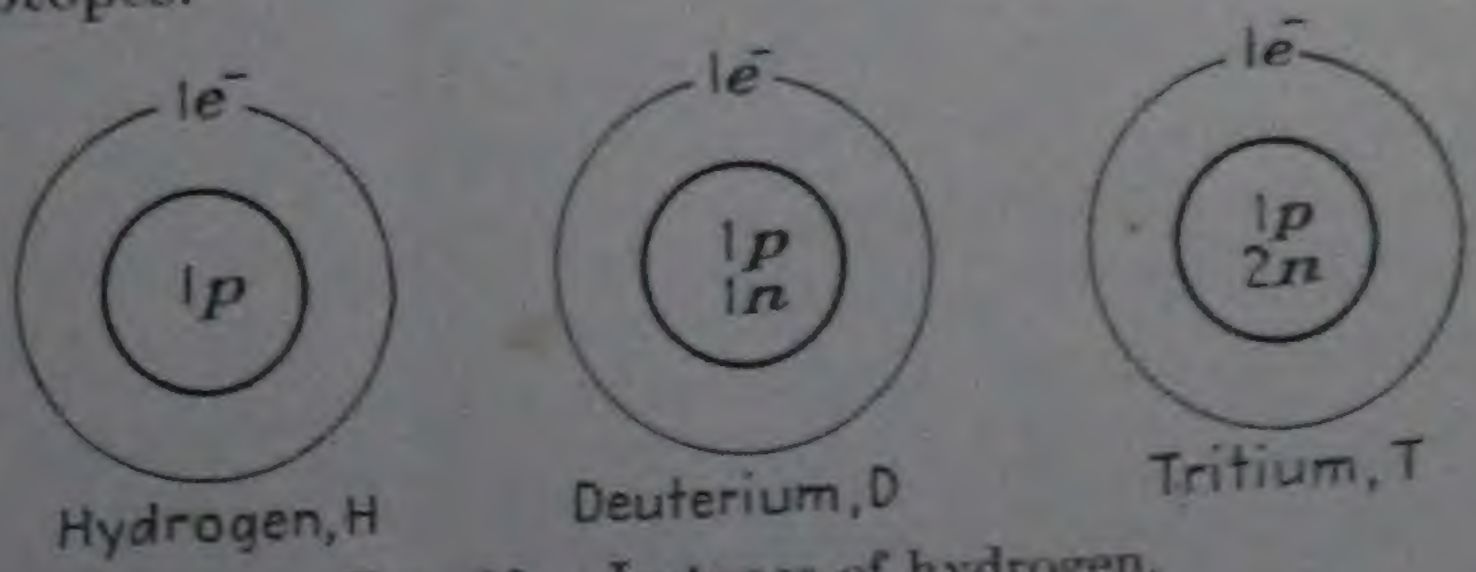

FIG. 20. Isotopes of hydrogen.

Heavy Water. The element hydrogen is known in the form of three isotopes having masses of one, two, and three; these are known as hydrogen (H), deuterium (D), and tritium (T), respectively. Incidentally, the element hydrogen is the only one for whose isotopes chemists and physicists have adopted separate names and symbols. Reference to Fig. 20 shows that these isotopes differ only with respect to the number of neutrons in the nucleus, and this of course accounts for the differences in mass.

Deuterium oxide (D_2O) represents a variety of water known as *heavy water*. As would be expected, this compound is chemically much the same as ordinary water (H_2O) but has somewhat different physical properties. For example, D_2O boils at 101.4° and melts at 3.8°, whereas H_2O boils at 100.0° and melts at 0°. Ordinary water contains D_2O to the extent of only 1 part in 6000. It is possible also to have a variety of water containing 1 atom of hydrogen and 1 atom of deuterium, another containing 2 atoms of tritium, one containing 1 atom of tritium and 1 atom of either hydrogen or deuterium, etc. In view of other possible combinations employing the known isotopes of oxygen, it follows that many different varieties of water having different isotopic compositions could be made.

Law of Constant Composition. The possibility of obtaining pure isotopes and using them to prepare pure compounds may appear to challenge the validity of the law of constant composition. It is obvious that the per cent oxygen in D_2O is less than that in H_2O. Similarly, from the isotopes of hydrogen and chlorine one could produce several different varieties of hydrogen chloride, and each would have a different percentage composition. However, each such pure compound should be considered as a separate chemical individual which, as such, conforms to the law. Furthermore, since the *average* atomic weight of each naturally occurring element is constant, the percentage composition of compounds derived therefrom is constant. It may therefore be concluded that the existence of compounds of different isotopic composition raises no serious problem so far as the law of constant composition is concerned.

Definition of the Term Element. Studies that have been pursued since the term *element* was first defined (Sec. 1.5) have led to the conclusion that certain of the elements are unstable in the sense that they undergo spontaneous radioactive change. Furthermore, it is recognized that some elements consist of atoms all of which are not alike, and these facts suggest that the previously stated definition may be somewhat ambiguous. Since the chemical properties of an element depend upon the extranuclear structure of its atoms, and because the extranuclear structure is related to the atomic number, the term element may be defined most satisfactorily in the following manner: **An element is a substance consisting entirely of atoms having the same atomic number.** This definition is entirely satisfactory in the sense that it implies no conflict with the existence of isotopes and the facts of radioactivity.

4.7. Compound Formation

Reference to Fig. 17 shows that, in the course of orderly development of the structures of the atoms of the elements, the first shell of electrons is completed in the helium atom. This is immediately followed (in lithium) with the beginning of the development of the second shell. The latter becomes completely filled in the neon atom, and thereafter the development of a third shell begins. Thus it is seen that the structures of helium, neon, and the other so-called *inert gases* are different from those of the atoms of all other elements in that their structures represent completely occupied shells. This condition is one of unusual significance because of the fact that such structures have the property of extreme chemical stability. The atoms of each inert gas have in their electron shells all of the electrons that can be accommodated, and these atoms are quite content to remain as they are. They show little if any tendency to enter into chemical reactions of any kind; they do not unite to form simple diatomic molecules or react with the atoms of other elements to form compounds. It is because of this striking degree of chemical inactivity that these elements are known as the *inert* gases.

Just as the exclusive presence of completed shells results in chemical inactivity, so the presence of a shell containing less than its maximum possible number of electrons is related to the tendency of the corresponding atoms to react to form molecules. In their reactions, these atoms tend to achieve the extranuclear structure of the inert gas which stands nearest in atomic number. The formation of molecules from atoms, therefore, may be looked upon as a manifestation of this tendency for each atom to achieve the stable arrangement and number of electrons that characterize the inert-gas structures. In the broadest sense there are three ways in which this may be accomplished:

1. Two or more atoms may combine by a process in which one kind of atom loses certain electrons and the other kind of atom gains these electrons. This process results in the formation of what is known as an *ionic compound*.

2. Chemical union may occur by a process in which two or more kinds of atoms share electrons, and the compounds so produced are said to be *covalent compounds*.

3. Compounds may be formed by a combination of the loss-gain and sharing processes. That is, two or more kinds of atoms may unite in a manner such that the chemical union is accomplished in part owing to loss and gain of electrons and in part owing to the sharing of electrons. Such compounds may be said to illustrate *intermediate types*

since they are intermediate between the extreme ionic and the extreme covalent types.

4.8. Ionic Compounds

The formation of an ionic compound by the loss and gain of electrons may be illustrated by the combination of lithium and fluorine. The neutral lithium atom has 1 electron in its outermost shell, and if it could lose this 1 electron, the resulting extranuclear structure would become like that of the nearest inert gas, helium. On the other hand, the neutral fluorine atom has 7 electrons in its outermost shell and can therefore achieve an extranuclear structure like that of the inert gas neon, provided that the fluorine atom can acquire the electron lost by the lithium atom, as shown in Fig. 21*a*. It should be observed that

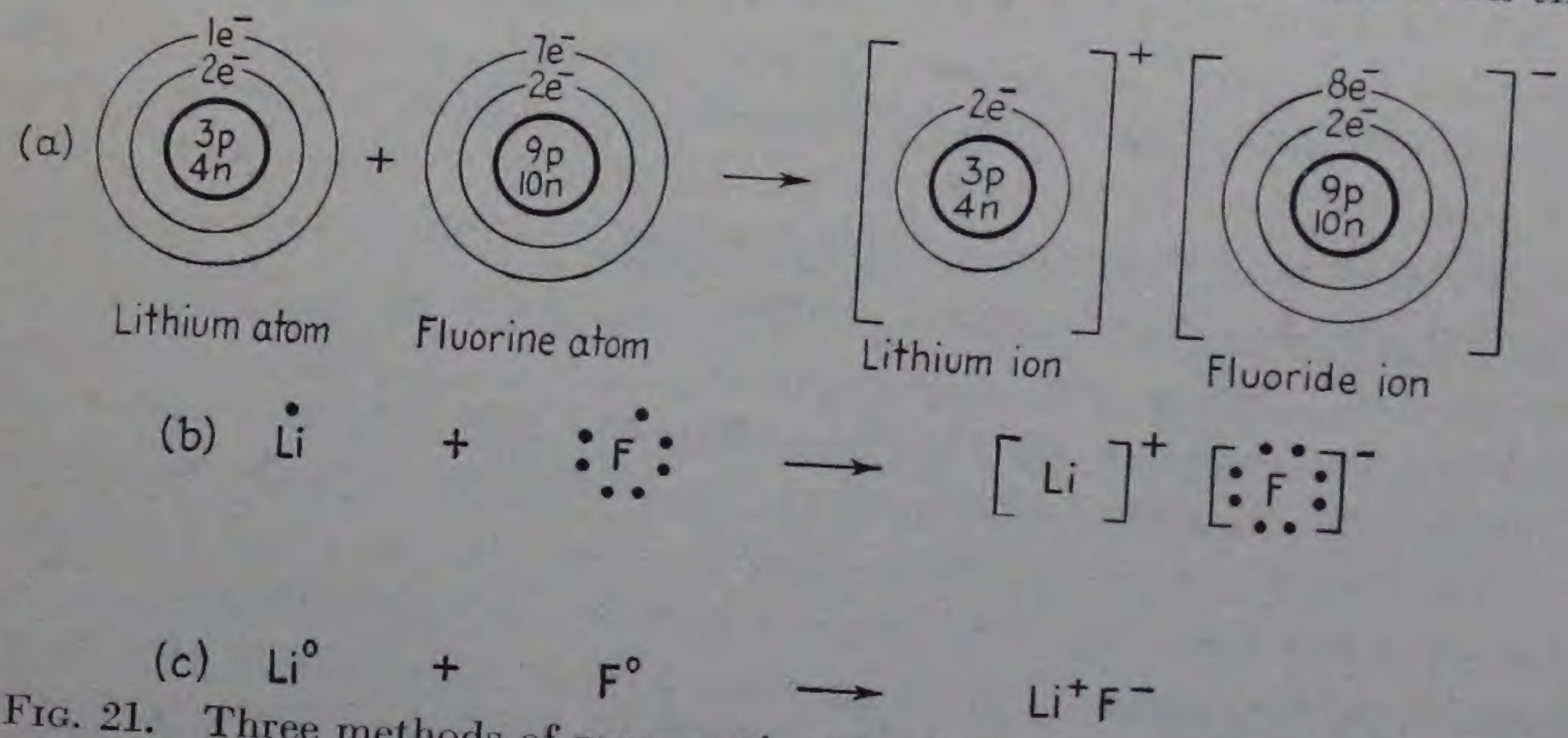

FIG. 21. Three methods of representing the formation of lithium fluoride.

the only parts of these two atoms that appear to be involved in this chemical change are the electrons in the outermost shells. Hence for convenience, one may equally well represent the reaction by using the symbols for the elements and surrounding these symbols by dots which represent the electrons in the outermost shells, as shown in Fig. 21*b*.

Ions. As is shown by Fig. 21*a*, the object that is formed when the neutral lithium atom loses an electron possesses an excess of 1 proton (*i.e.*, 3 protons and 2 electrons) and hence is not an electrically neutral body. An atom (or radical) that bears an electrical charge is called an *ion*. Thus a *positive ion* is formed when a neutral lithium atom loses an electron, and a *negative ion* is formed when a neutral fluorine atom gains an electron. It follows that the combination of lithium and fluorine may be represented as shown in Fig. 21*c*, in which the zero superscripts represent the electrical neutrality (zero charge) of the

original atoms and in which the ions of the compound, lithium fluoride, are represented as being held together by the attraction of their unlike charges. It follows that ions must be produced when atoms lose and gain electrons; hence the name, *ionic* compounds.

Figures 21*a*, *b*, and *c* represent merely three different methods of describing the same reaction and differ only to the extent to which they provide detailed information. Additional examples of the schematic representation of the formation of ionic compounds are given in Fig. 22.

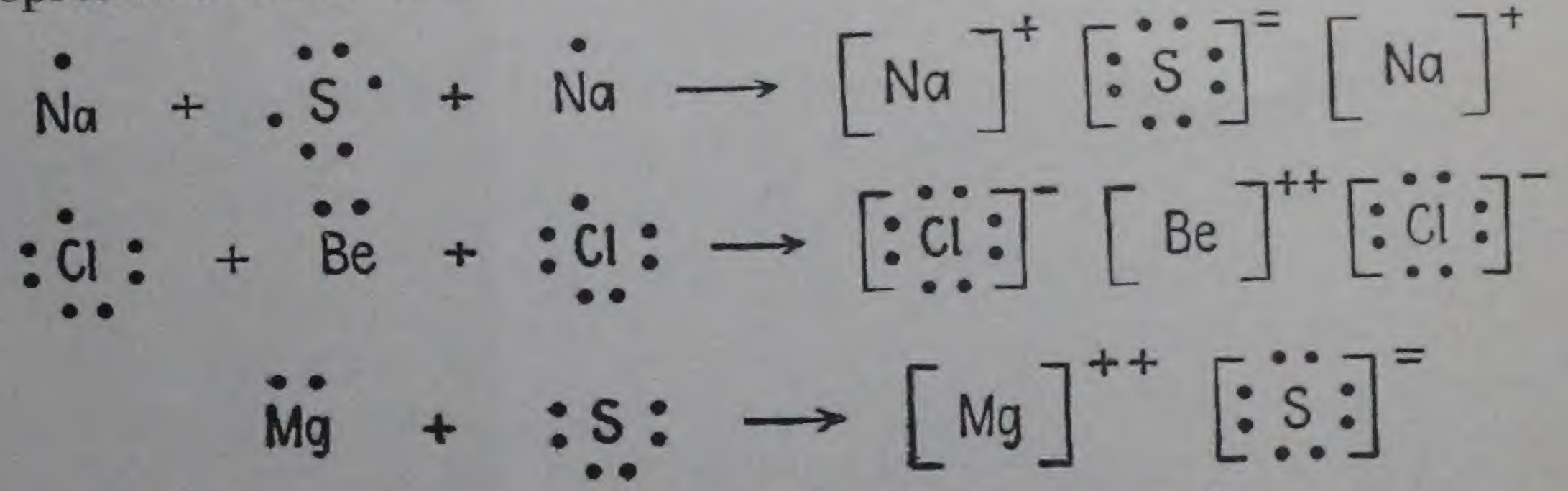

FIG. 22. The formation of ionic compounds.

Oxidation and Reduction. The loss of one or more electrons by an atom (or a group of atoms) is called *oxidation*, and the atom or atoms that lose electrons are said to be *oxidized*. Similarly, the gain of electrons is known as *reduction*, and the atom or atoms that gain electrons are said to be *reduced*. The processes of oxidation and reduction always occur together in a manner such that the number of electrons lost and the number gained are the same. Because of this mutual interdependence, the substance which gains electrons is called the *oxidizing agent*, since by gaining electrons it makes it possible for another substance to lose electrons. The *reducing agent*, on the other hand, is that which loses electrons and thereby makes possible the occurrence of the reduction reaction. Thus, in any oxidation-reduction process, the oxidizing agent is reduced and the reducing agent is oxidized.

So far as the reactions of inorganic substances are concerned, oxidation-reduction reactions constitute the most common and most important type of chemical change. Reactions in this category are considered from a somewhat broader viewpoint and in more detail in Chap. 17.

4.9. Covalent Compounds

The formation of the covalent compound water is represented by Fig. 23. Each hydrogen atom requires one additional electron in

order to achieve a structure similar to that of helium, while the oxygen atom needs two additional electrons in order to acquire an extranuclear structure similar to that of the neon atom. These requirements are met if each hydrogen atom shares its 1 electron with oxygen while, at the same time, each hydrogen atom is permitted to share one of the electrons originally belonging to the neutral oxygen atom. This type of chemical union may be thought of as involving an "overlapping of

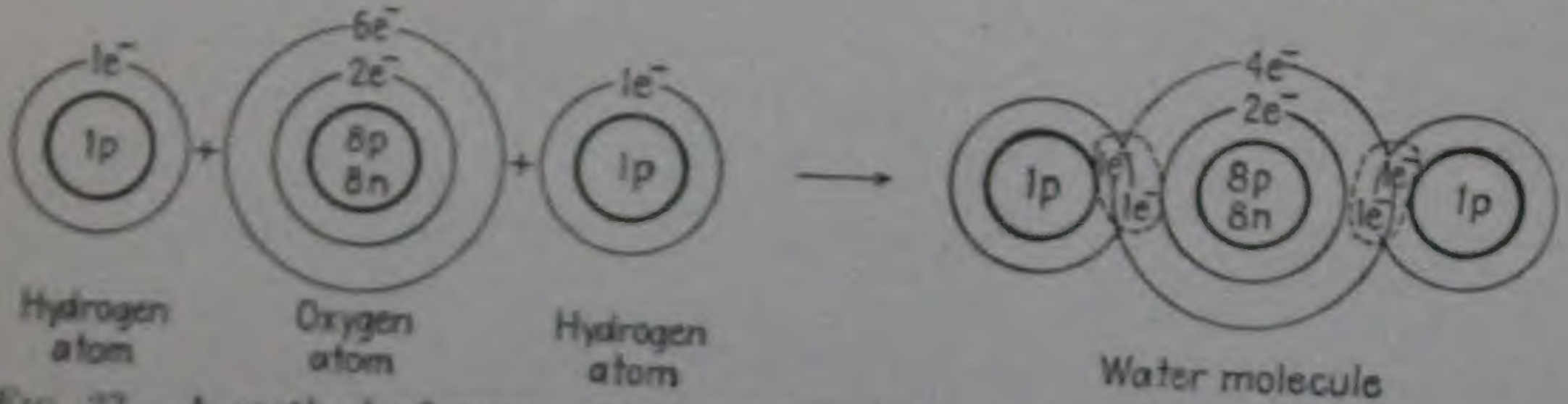

Fig. 23. A method of representing the formation of water from hydrogen and oxygen.

shells" in which the union is established by a "shared pair of electrons" (shown surrounded by dotted lines in Fig. 23) and in which this pair rotates at the same time in the outermost shells of both the atoms concerned. In effect, the oxygen atom now has 8 electrons rotating in its outermost shell while, simultaneously, 2 electrons are functioning in the shells of each of the 2 hydrogen atoms, and each kind of atom has achieved structural similarity to the nearest inert gas. Since this appears to be a situation involving no actual loss and gain of electrons, it follows that ions are not formed in the process of the establishment of a true covalent combination.

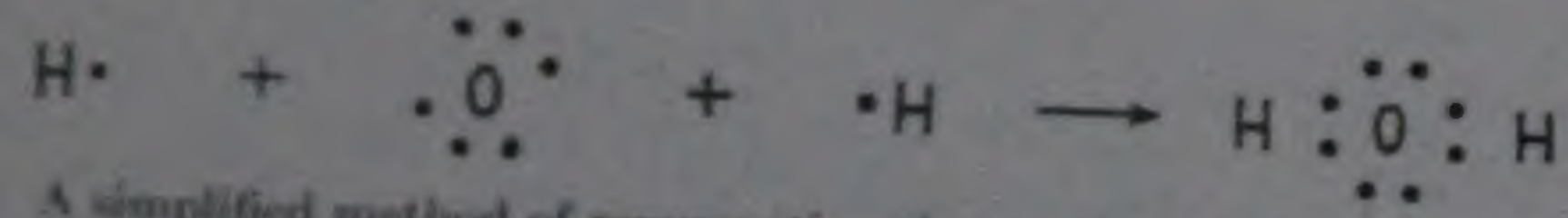

Fig. 24. A simplified method of representing the covalent union of hydrogen and oxygen.

Again, it is seen that only the electrons in the outermost shells are involved; consequently, the reaction may be represented as shown in Fig. 24. Another example of a covalent combination is shown in Fig. 25, in which 1 atom of carbon is shown in combination with 1 atom of hydrogen and 3 of chlorine in the covalent compound chloroform.

Elemental Gas Molecules. The molecules of most elemental gases are known to contain *at least* 2 atoms each (Sec. 8.3). In the light of the preceding ideas, the structures of these molecules may now

be represented diagrammatically, as shown in Fig. 26. These cases provide additional examples of covalent combination. From these diagrams, one may also see that at least 2 and *only* 2 atoms need to be involved in each molecule. Since, upon forming a covalent union, any two such atoms possess enough electrons so that, by sharing, the

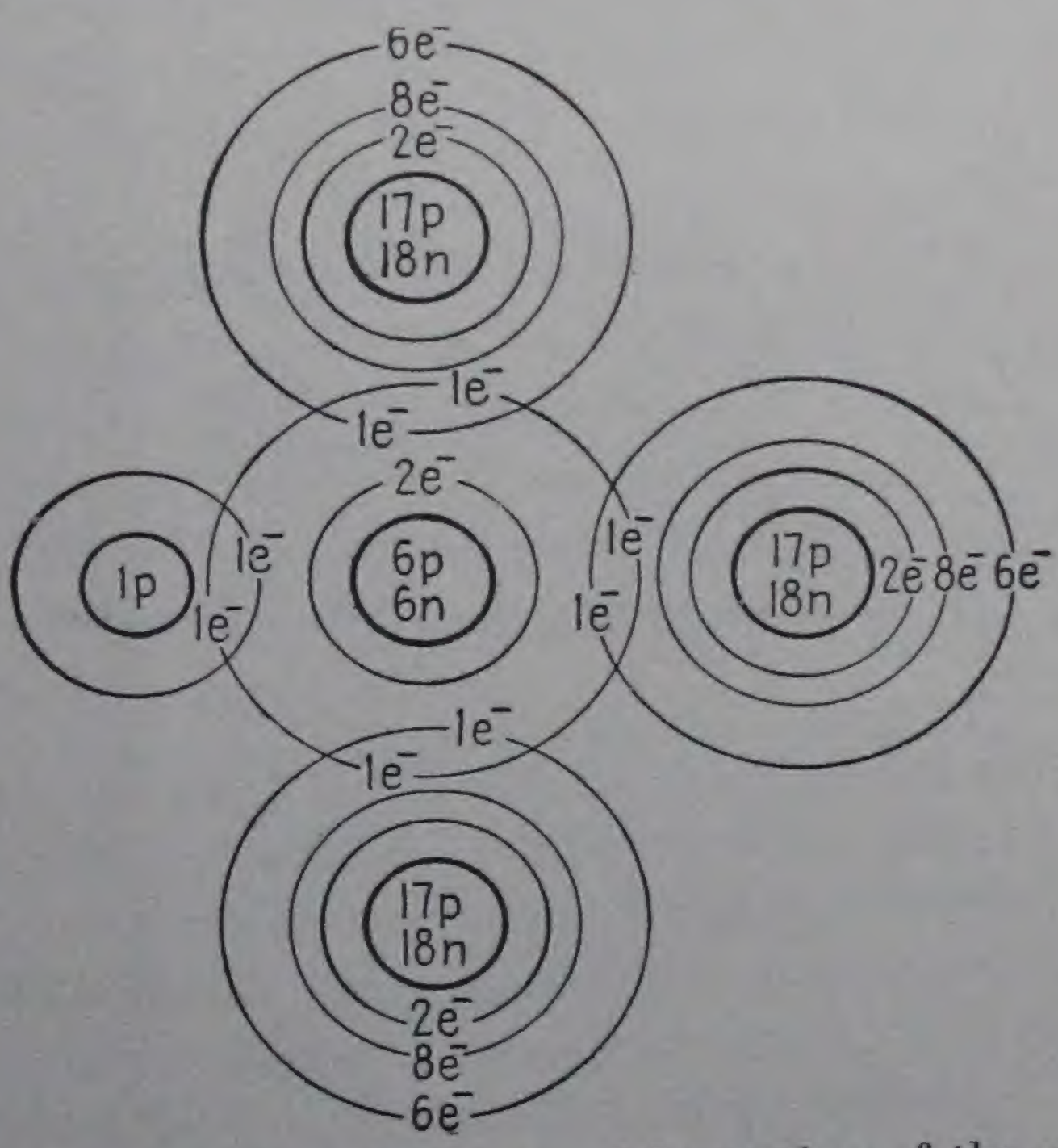

FIG. 25. Diagram illustrating the mode of formation of the covalent compound chloroform, $CHCl_3$.

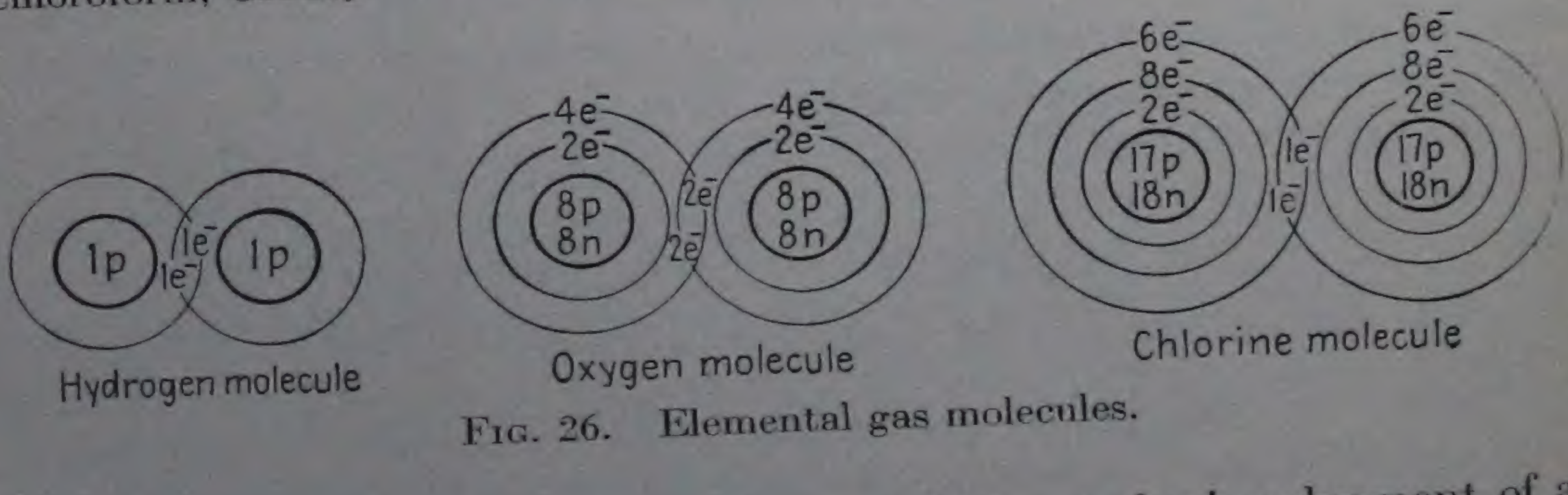

FIG. 26. Elemental gas molecules.

requirements of each atom can be met without the involvement of a third atom. In the cases of hydrogen and chlorine, the mutual utilization of only one pair of electrons (1 from each atom) is all that is necessary, while in the case of oxygen a total of 4 electrons (2 from each atom) is required if each oxygen atom is to achieve a stable inert-gas structure. Similar diagrams may be drawn to represent the molecules of gases such as nitrogen or fluorine.

4.10. Intermediate Types

As has already been suggested in the preceding section, molecules may be formed in a manner such that both "loss-gain" and "sharing" of electrons contribute simultaneously to the establishment of the chemical union. Thus, between the strictly ionic and the strictly covalent types of compound, there is possible a wide variety of so-called *intermediate* types. Such compounds are commonly designated in terms of the process that is involved to the greater extent. For example, if a compound is formed largely by the loss-gain process, the compound is said to be predominantly ionic. Similarly, predominantly covalent compounds are those in which the process of sharing of electrons plays the major role. Although no effort need be made here to represent the structures of intermediate types, it is of importance to recognize the existence of such compounds, which, after all, constitute the great majority of known inorganic chemical substances.

4.11. Valence

Long before chemists had any well-defined ideas about the manner in which chemical combination occurs, there was needed some means of expressing the combining power or combining capacity of each kind of element. It was necessary to have some way of expressing, for example, the fact that in a given reaction 1 atom of zinc is capable of displacing 2 atoms of hydrogen; that 1 atom of nitrogen can combine with 3 atoms of hydrogen, etc. This led to the development of the concept of *valence*, in which small whole numbers represent the capacity of one element to combine with (or displace) other elements. Thus, the valence of nitrogen was said to be 3 because 1 atom of nitrogen can combine with 3 atoms of hydrogen, each of which has unit valence. Similarly, zinc was said to have a valence of 2 because 1 atom of zinc displaces 2 atoms of hydrogen.

The more that is learned about the actual manner in which chemical changes occur, the less is the need for any designation of valence. In the case of the predominantly covalent ammonia (NH_3) molecule, for example, the valence of nitrogen is 3 because three chemical bonds exist between the nitrogen atom and the three hydrogen atoms, and each is established by the sharing of a pair of electrons. The valence of hydrogen in the same compound is 1 for the reason that each hydrogen atom is involved in only one shared pair of electrons. The valence of zinc is also apparent from an understanding of the nature of the reaction which has the following essential features:

$$Zn + 2H^+ \rightarrow Zn^{++} + H_2$$

The zinc atom loses 2 electrons and becomes a dipositive zinc ion; hence the valence of zinc is 2. Each hydrogen ion gains 1 electron (consequently, the valence of hydrogen is 1), and the two resulting neutral hydrogen atoms share electrons to form a covalent hydrogen molecule, H_2.

Electrovalence and Covalence. In terms of the two processes that may be concerned in the formation of molecules, it is necessary to recognize at least two kinds of valence, *viz.*, electrovalence and covalence.

The number of electrons lost or gained is taken as a measure of electrovalence, which is designated as positive or negative depending upon whether a positive or negative ion is formed. For example, if a calcium atom loses 2 electrons, it is said that the resulting calcium ion has a positive valence of two; and if those 2 electrons are gained by a sulfur atom, the resulting sulfur ion has a negative valence of two.

The total number of pairs of electrons shared by a given atom in a molecule is a measure of the covalence of that atom. Thus, in the covalent compound SiF_4, the silicon atom has a share in four pairs of electrons and is therefore said to have a covalence of four. *Each* fluorine atom, however, has a share in only one pair of electrons and consequently has a covalence of one. Similarly in the water molecule (Fig. 23) oxygen has a covalence of two and hydrogen a covalence of one.

Equivalence. The foregoing ideas make possible a clearer understanding of the weight relationships that are involved in chemical changes (Chap. 2). It should be recalled that equivalent weights were expressed in terms of 8 g. of oxygen, and it is now clear that the oxygen atom tends to gain or share 2 electrons so as to have 8 electrons in its outermost shell. One gram-atom of oxygen (16 g.) therefore corresponds to a 2-electron change, whereas one-half gram atom of oxygen (8 g.) bears the same relationship to a 1-electron change. On the relative weight basis of O = 16 (which is necessary only to avoid a relative atomic weight less than unity for hydrogen), 1 gram-atom of hydrogen similarly is that which is involved in a 1-electron change.

It is apparent that an equivalent weight of any element is that which corresponds to a change involving 1 electron per atom of that element. The electron concerned in the change may be either lost, gained, or shared, or it may be involved in a combination of these processes. Consequently, since valence expresses the total number of electrons which the atom loses, gains, or contributes to the sharing process, the equivalent weight of an element in any compound may be found by

dividing the atomic weight by the valence which the element exhibits in that compound. Thus, in the case of NH_3, the equivalent weight of nitrogen is $14.008/3 = 4.669$.

GENERAL EXERCISES

1. List the fundamental particles of which all atoms are composed and indicate the mass and charge of each.
2. Why is the chemist usually more interested in the extranuclear structures of the atoms than in the composition of their nuclei?
3. In terms of the structures of atoms, what is the significance of atomic numbers?
4. Identify each of the following and describe briefly the nature and properties of each: (*a*) α-particle, (*b*) γ-ray, (*c*) β-particle.
5. By referring only to the list of atomic weights and atomic numbers given on the inside front cover of this book (and without referring to any of the diagrams given in this or any other chapter), draw complete diagrams representing the structures of the elements having atomic numbers 1 to 20 inclusive.
6. Distinguish between the following terms: (*a*) atom and ion, (*b*) electrovalence and covalence, (*c*) oxidation and reduction.
7. In what way may atoms unite to form molecules?
8. What is the essential difference between an ionic compound and a covalent compound?
9. By means of suitable diagrams, represent the complete structures of (*a*) the ionic compounds $CaCl_2$, KF, Mg_3P_2, Na_3N, and (*b*) the covalent compounds CH_4, SiH_2Cl_2, CCl_2F_2, SF_6.
10. Show three ways of representing the formation of the ionic compound calcium fluoride (CaF_2).
11. Show two different means of representing the formation of 1 molecule of nitrogen from 2 atoms of nitrogen.
12. Explain the meaning of the following terms: (*a*) isotope, (*b*) reducing agent, (*c*) heavy water, (*d*) oxidizing agent.
13. Why are the isotopes of an element not considered to be separate elements?
14. Two isotopes of boron (atomic number = 5) exist in nature; these have masses of 10 and 11. Draw diagrams representing the structures of these isotopes.
15. Draw diagrams representing the three isotopes of silicon which have masses of 28, 29, and 30. The atomic number of silicon is 14.

SUGGESTED READING

Journal of Chemical Education

Conant, Atoms, Molecules, and Ions, **5**, 25 (1928).
Standen, Why Do We Believe in Electrons?, **23**, 356 (1946); **24**, 120 (1947).
Shadduck, The Neutron, **13**, 303 (1936).
Selwood, Heavy Water, **18**, 515 (1941).
Eidinoff, The Search for Tritium—The Hydrogen Isotope of Mass Three, **25**, 31 (1948).
Standen, The Fairy Story of Valence, **24**, 481 (1947).

CHAPTER 5

PREPARATION AND PROPERTIES OF OXYGEN; THERMOCHEMISTRY

Of the known chemical elements, oxygen is by far the most abundant and certainly one of the most important. Elemental oxygen is present in air to the extent of approximately 21 per cent and makes up more than 50 per cent of the earth's crust. This element also constitutes a significant part of such familiar materials as wood, ores, cotton, and foodstuffs. Oxygen and compounds of oxygen are essential in such important processes as animal and plant respiration, the burning of fuels, the corrosion or rusting of metals and alloys, and the decay of animal and vegetable matter. Historically, the English clergyman Priestley (Fig. 27) is commonly credited with the discovery of oxygen. There is ample evidence, however, to indicate that this element was first prepared and recognized as an elemental substance by the Swedish chemist Scheele (Fig. 28).

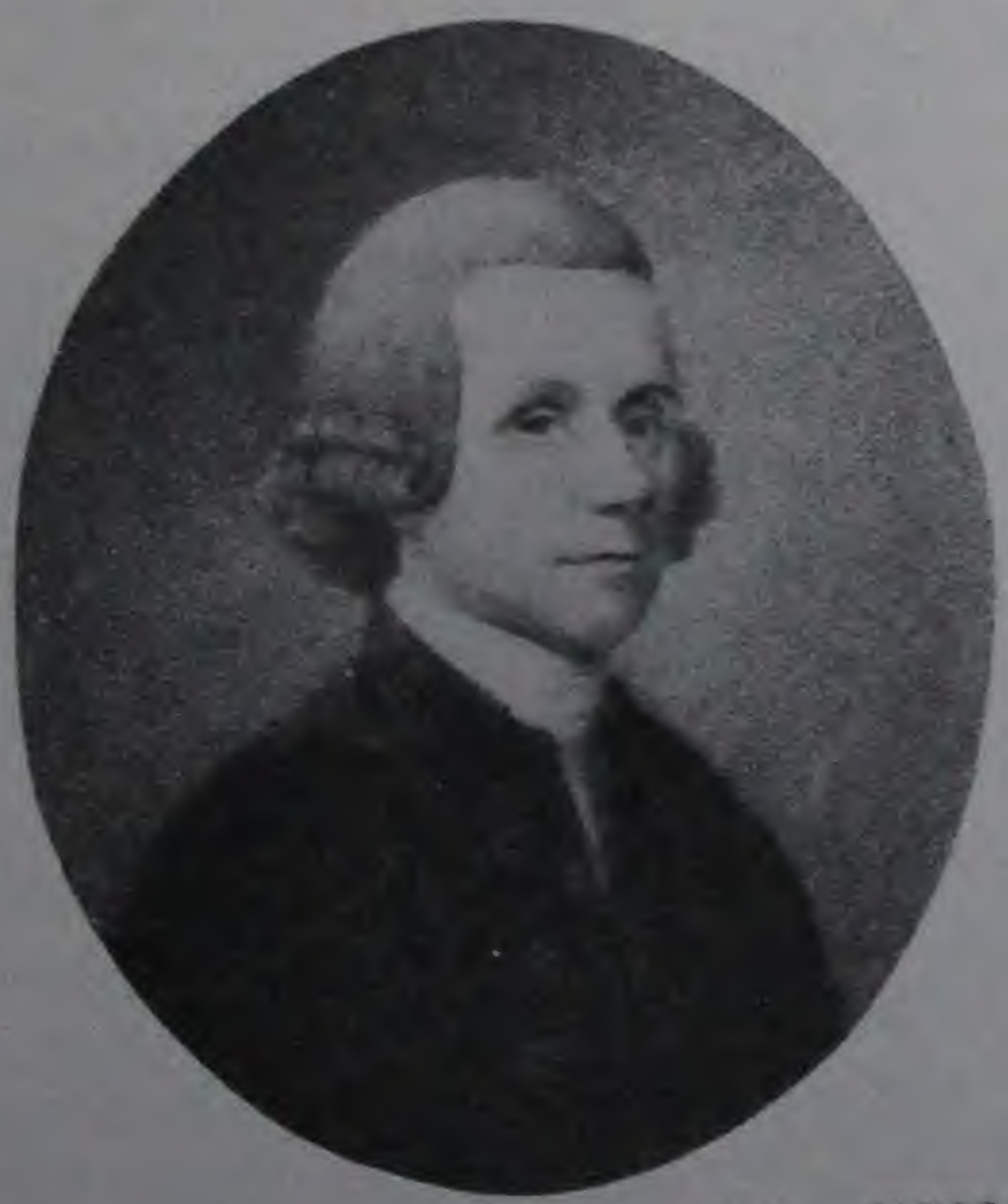

FIG. 27. Joseph Priestley (1733–1804). (*Courtesy of The Edgar Fahs Smith Memorial Collection in the History of Chemistry, The University of Pennsylvania.*)

5.1. Preparation of Oxygen

Methods for the production of elemental or compound substances may be classified as (*a*) laboratory methods and (*b*) commercial methods. The choice of procedure employed in any given instance is governed by numerous factors such as the quantity and the purity of the material required, cost, and convenience. For small-scale use in the laboratory, methods which result in pure products and which are convenient are usually preferred regardless of the cost involved.

Separation of Oxygen from Air. Dry air is a mixture consisting

of roughly 21 per cent oxygen and 78 per cent nitrogen by volume. The remaining 1 per cent consists of carbon dioxide (CO_2) and a group of elements which are usually referred to as "the inert gases of the atmosphere," *viz.*, helium (He), neon (Ne), argon (A), krypton (Kr), and xenon (Xe).

Under suitable experimental conditions, air may be caused to liquefy. When the resulting liquid mixture is allowed to boil, the various components pass from the liquid to the gaseous state at different temperatures. After a quantity of "liquid air" has been allowed to boil until a little more than four-fifths has vaporized, the liquid that remains is oxygen of sufficient purity for most industrial uses. The greater part of the oxygen sold commercially is secured from the air.

FIG. 23. Karl Wilhelm Scheele (1742–1786). (*Courtesy of The Edgar Fahs Smith Memorial Collection in the History of Chemistry, The University of Pennsylvania.*)

Preparation of Oxygen by the Decomposition of Water. Water is a cheap, abundant "raw material" which is exceptionally rich in oxygen (nearly 90 per cent by weight). By subjecting water to the action of an electric current, water may be decomposed as shown by the equation

$$2H_2O \rightarrow 2H_2 + O_2$$

This method for the production of oxygen is adaptable to both laboratory and commercial-scale use.

Preparation of Oxygen by the Decomposition of Other Compounds of Oxygen. The most convenient method for the production of pure oxygen on a laboratory scale involves the thermal decomposition of certain compounds that contain oxygen. It has already been shown that oxygen is liberated when potassium chlorate is decomposed by heat. In a similar manner, other compounds containing oxygen may be decomposed. It should not be inferred, however, that all compounds of oxygen are decomposed with the liberation of elemental oxygen. Many such compounds, when heated, give up only a part of their oxygen, while still others yield products other than the element oxygen.

There are given below five equations representing reactions that yield oxygen gas. All these reactions require that the solid reactants be heated to elevated temperatures, which differ depending upon the particular compound used as the source of oxygen.

$$\underset{\text{Mercuric oxide}}{2HgO} \rightarrow 2Hg + \overline{O}_2$$

$$\underset{\text{Lead dioxide}}{2PbO_2} \rightarrow \underset{\text{Lead monoxide}}{2PbO} + \overline{O}_2$$

$$\underset{\text{Manganese dioxide}}{3MnO_2} \rightarrow \underset{\text{Manganous-manganic oxide}}{Mn_3O_4} + \overline{O}_2$$

$$\underset{\text{Potassium nitrate}}{2KNO_3} \rightarrow \underset{\text{Potassium nitrite}}{2KNO_2} + \overline{O}_2$$

(It is not necessary that the student memorize these or other equations. When the names and formulas of the reactants and products have been learned, the equations may be written by application of the method previously outlined.)

5.2. Catalysis

When white solid crystals of pure potassium chlorate are heated, the solid melts when the temperature reaches 200°C. At this temperature, however, oxygen is not liberated at any appreciable rate. In order for the decomposition to occur rapidly, it is necessary to raise the temperature above 360°. If to pure potassium chlorate there is added a very small quantity of manganese dioxide, it is found that the $KClO_3$ is decomposed rapidly at about 200°. That is, in the presence of a foreign substance, manganese dioxide, the rapid decomposition of potassium chlorate occurs at a considerably lower temperature than that required in the absence of the foreign substance. Consider the two parallel situations:

$$\text{At } 200°\text{C.} \begin{cases} KClO_3 \text{ alone decomposes very } \textit{slowly} \\ KClO_3 \text{ in the presence of } MnO_2 \text{ decomposes } \textit{very rapidly} \end{cases}$$

Before this striking result can be explained, it is necessary also to know that upon completion of the decomposition of the $KClO_3$, the MnO_2

can be recovered unchanged. As far as can be ascertained, the MnO_2 is the same material in every respect as that originally mixed with the potassium chlorate and has not been altered in any way. The MnO_2, however, by virtue of its presence is seen to be capable of speeding up the decomposition of potassium chlorate. This is an example of catalytic action or *catalysis*. A similar result would have been obtained by using ferric oxide (Fe_2O_3) or potassium dichromate ($K_2Cr_2O_7$) in place of the manganese dioxide. The use of manganese dioxide as a catalyst for the preparation of oxygen by the decomposition of potassium chlorate may appear to be subject to criticism on the grounds that MnO_2 will itself yield oxygen when heated. Such criticism is rendered invalid by the fact that the decomposition temperature of manganese dioxide is much higher (535°C.) than the temperature employed in the catalyzed decomposition of $KClO_3$ and by the fact that, after use as a catalyst, the MnO_2 can be recovered unchanged.

In addition to substances that accelerate certain chemical reactions there are some that decrease the rates of certain reactions. The presence of a foreign substance that is not itself consumed in the reaction may result in (1) an increase, (2) a decrease, or (3) no change in the rate of a given reaction. Accordingly, **a catalyst may be defined as a substance which alters the rate of a chemical reaction and which is not consumed in the reaction.** It is becoming increasingly common to restrict the term *catalysl* to those substances which increase the rates of reactions and to describe those which decrease reaction rates as *retarders* or *inhibitors*.

In general, catalysts and retarders are very specific in their behavior. A substance that catalyzes one reaction may be wholly without effect in another reaction. Similarly, a material that is a catalyst for one particular reaction may act as an inhibitor for another. The entire subject of catalysis is one of the most intriguing and least understood phases of the science of chemistry.

Applications of Catalysis. In connection with commercial chemical processes, applications of both catalysts and inhibitors are numerous. In fact, many important industrial products are available at low cost only because of catalytic action. Finely divided platinum, ferric oxide, vanadium pentoxide (V_2O_5), and oxides of nitrogen are used to accelerate the combination of sulfur dioxide and oxygen in the manufacture of sulfuric acid. One method for the commercial production of ammonia (NH_3) depends upon the fact that the union of nitrogen and hydrogen is catalyzed by metals such as platinum or uranium. Liquid vegetable oils such as cottonseed oil are changed into semisolid

substitutes (such as Crisco, Snowdrift, or Spry) for animal fats by reaction with hydrogen in the presence of a catalyst consisting of finely divided nickel.

There are also many examples of the use of inhibitors. Many food and drug products deteriorate when exposed to the air unless suitable inhibitors or retarders, such as sodium benzoate, are added. The useful life of articles made of rubber is increased by the presence of retarders which decrease the rate at which the rubber is attacked by atmospheric oxygen.

5.3. Properties of Oxygen

Under ordinary conditions of temperature and pressure, oxygen is a colorless, odorless gas which is slightly heavier than air and which dissolves in water at room temperature to the extent of only 3 volumes of oxygen per 100 volumes of water. When cooled to -182.963°C., oxygen passes from the gaseous to the liquid state. Liquid oxygen has a steel-blue color and is highly magnetic. At -218.4°C., liquid oxygen solidifies. Other properties which may be listed here and the significance of which is explained later are boiling temperature $= -182.963$°C.; melting temperature $= -218.4$°C.; critical temperature $= -118.8$°C. (see Sec. 6.1); density $= 0.0014292$ g. per cc. All the properties mentioned thus far are of the type known as *physical properties*. There are also those properties which are known as *chemical properties*. The chief chemical property of oxygen is its tendency to combine with other elements to form compounds known as *oxides*. It has already been pointed out that under ordinary conditions oxygen gas consists of covalent molecules containing 2 atoms each.

5.4. Uses of Oxygen

The annual production of oxygen in the United States amounts to approximately 14,000 million cubic feet, most of which is obtained from liquid air. The bulk of this oxygen is used in the production of high temperatures in the burning of gaseous fuels such as acetylene in the oxyacetylene torch, which is used in the cutting and welding of metals and alloys. Minor uses center about the problem of supplying adequate oxygen for human respiration under conditions where the quantity of oxygen in the atmosphere is insufficient. Thus, portable tanks of oxygen are carried by aviators for use at very high altitudes, by mine rescue squads following explosions, by the crews of submarines that must remain submerged over considerable periods of time, and by

divers engaged in undersea work. The physician frequently administers oxygen in the treatment of respiratory ailments, such as pneumonia.

5.5. Ozone

When pure dry oxygen or dry air is passed between two electrically charged plates arranged as shown in Fig. 29, a portion of the oxygen is converted to a substance known as *ozone*, which has the formula O_3.

$$3O_2 + \text{energy} \rightarrow 2O_3$$

During storms, small traces of ozone are produced in the atmosphere by lightning discharges. At ordinary temperatures, ozone is a pale-

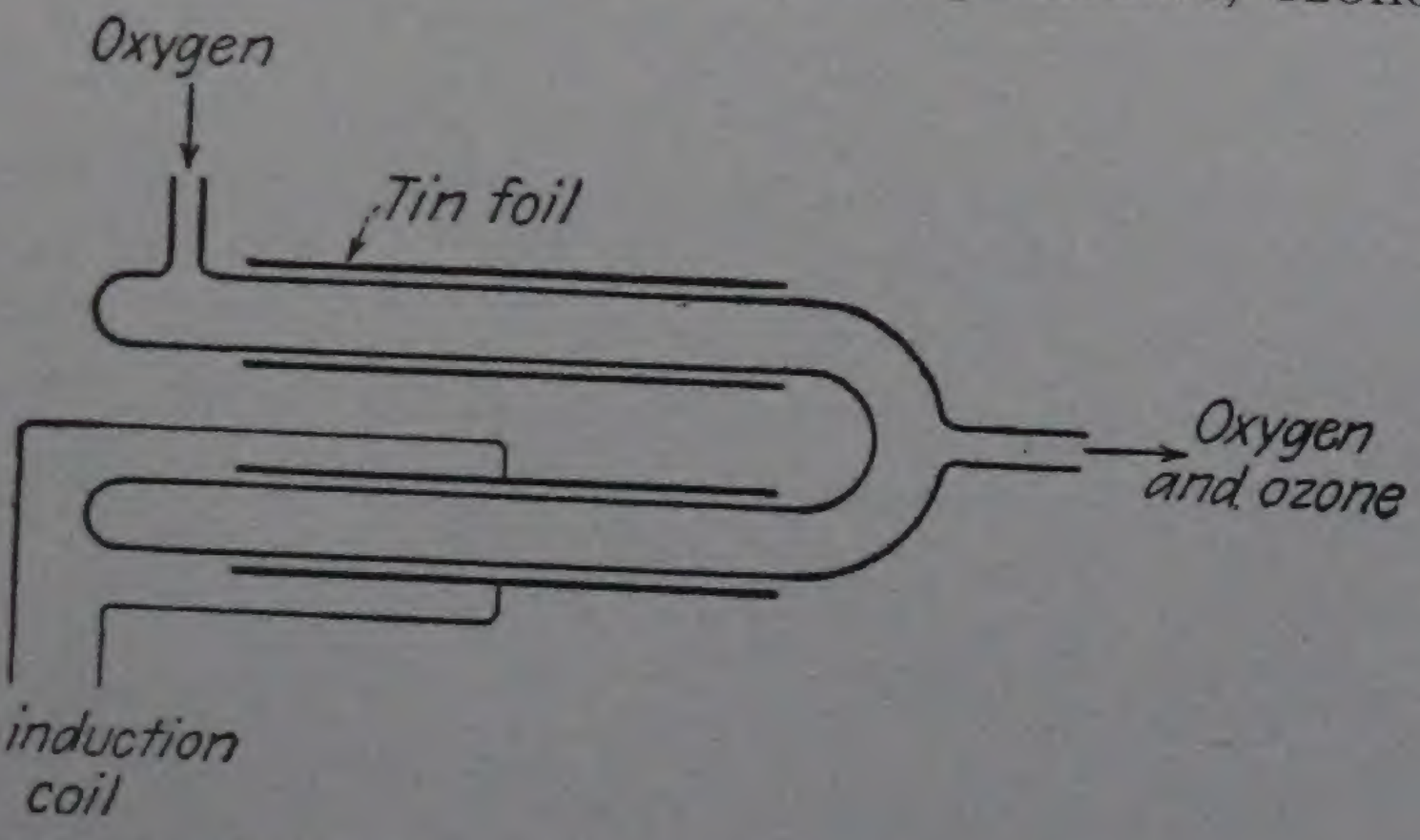

FIG. 29. Apparatus for the preparation of ozone by the method of Siemens.

blue gas having a characteristic "fresh" odor. It is about 1.5 times as heavy as ordinary oxygen and is much more active chemically, as is shown by the fact that it combines readily with metals such as silver and mercury which unite with ordinary oxygen only very slowly. Ozone is very unstable and decomposes into ordinary oxygen,

$$2O_3 \rightarrow 3O_2$$

a reaction which proceeds rapidly at elevated temperatures and which is catalyzed by water vapor. Pure ozone decomposes with explosive violence. Because of the difficulty and high cost of producing ozone, the pure substance is not used commercially; however, air containing appreciable quantities of ozone ("ozonized air") is used for the sterilization of drinking water. Ozonized air has also been used to a limited extent as a bleaching agent, as a deodorizer, and as a disinfectant.

The existence of an elemental substance in two or more forms having distinctly different properties is not uncommon. These different forms are called *allotropic modifications* of the element. The element

oxygen is one that exhibits *allotropy* since the two allotropic modifications, O_2 and O_3, are known. Several of the nonmetals and metals exhibit allotropy, and certain of these cases are considered later in some detail.

5.6. Combustion

All the elements excepting the inert gases combine with oxygen to form oxides. These oxides are classified as *binary* compounds since they contain only two kinds of elements. Thus, **an oxide may be defined as a binary compound which contains the element oxygen.** This process of combination with oxygen is another example of *oxidation*,[1] and the substance that unites with oxygen is said to be *oxidized*. The union of elements (or of compounds) with oxygen is accompanied by either the absorption or the liberation of energy in the form of heat. The oxidation of a given quantity of matter involves the same quantity of heat (liberated or absorbed) regardless of the rate at which the oxidation occurs. **Rapid oxidation accompanied by the liberation of energy in the form of heat and light is called combustion.**

When heat is liberated in an oxidation reaction, the atmosphere and surrounding objects absorb the liberated heat, with the result that the temperature of the material undergoing oxidation does not become very high. If, however, the substance being oxidized is so insulated that the heat evolved cannot escape readily, the temperature may increase to such an extent that the substances burst into flame, *i.e.*, *spontaneous combustion* occurs. Oil-soaked rags frequently are involved in spontaneous combustion because the oil oxidizes slowly and the rags provide insulation which prevents the escape of the heat liberated. As the heat accumulates, the temperature is increased and the oxidation proceeds progressively more rapidly until finally the ignition temperature of the mass is reached and it bursts into flame.

5.7. Production and Uses of the Inert Gases of the Atmosphere

Although the inert gases are present in the atmosphere only to the extent of about 1 per cent (by volume), methods have been devised whereby helium, neon, argon, krypton, and xenon may be obtained in a fair degree of purity. These gaseous elements, which were discovered by the English chemist Ramsay and his co-workers, are unique among

[1] As shown in Chap. 4, the term oxidation is one broadly applicable to a class of reactions in which practically all of the elements may participate. The term is in no sense limited to reactions in which the element oxygen is involved.

the chemical elements in that these inert gases exhibit little or no tendency toward entering into chemical combination. Since these elements are inactive chemically, they must be separated and purified by physical rather than by chemical methods.

Helium is obtained from natural gas in plants owned and operated by the government and located in Kansas and Texas (Fig. 30). The gases from certain wells in this region contain considerable quantities of nitrogen and approximately 1 per cent helium. The latter is separated

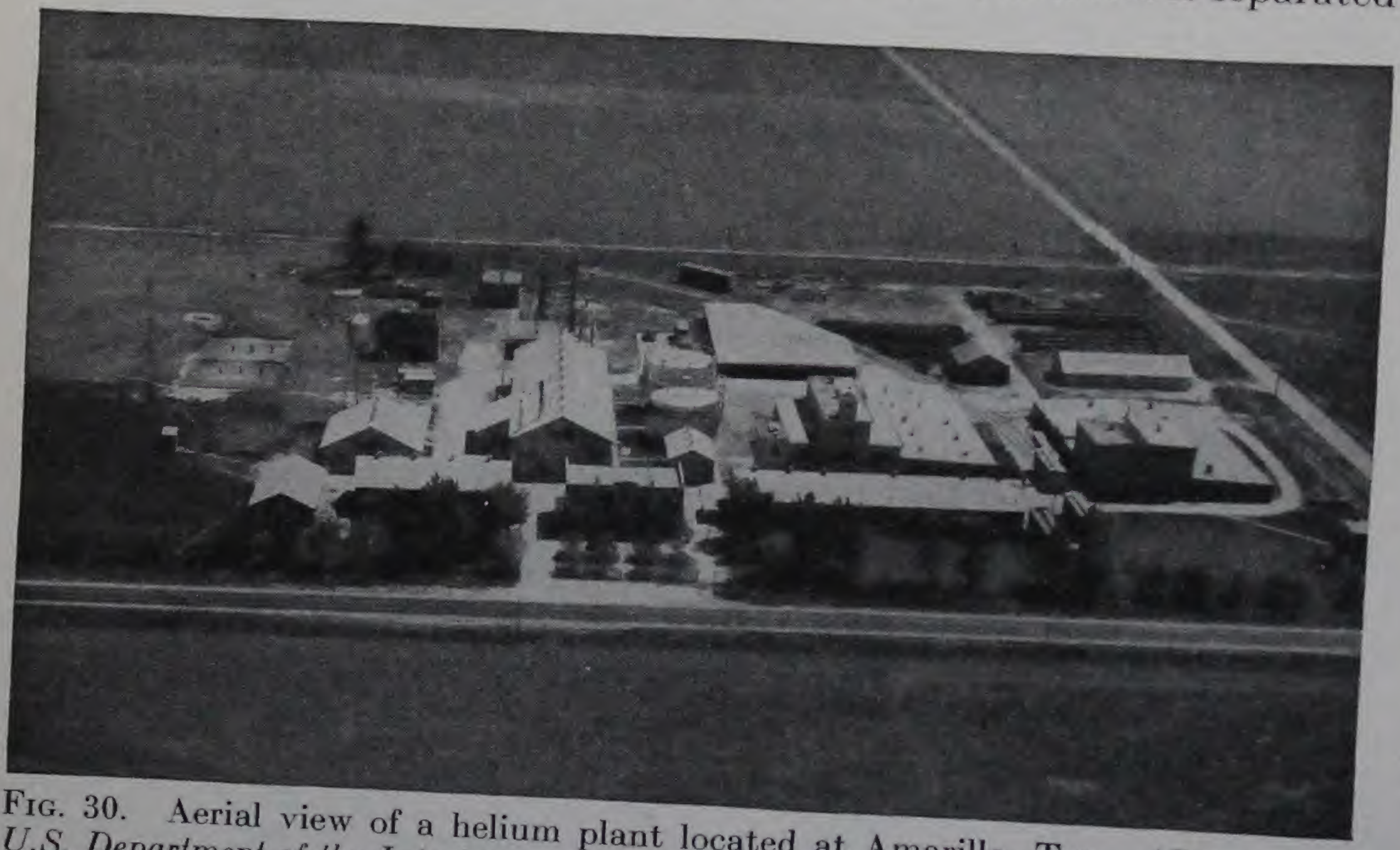

FIG. 30. Aerial view of a helium plant located at Amarillo, Tex. (*Courtesy of U.S. Department of the Interior, Bureau of Mines.*)

by liquefying all the other gases, and the gaseous helium (which boils at the very low temperature of $-268.90°C.$) is then separated from the other liquefied gases. In this manner about 30 million cubic feet of helium are produced annually at a cost of only a few cents per cubic foot, whereas, in 1918, the use of less efficient methods involved a production cost of approximately $2500 per cubic foot. Helium is used chiefly in the inflation of observation balloons and other lighter-than-air craft. Its advantage over hydrogen for this purpose lies in the fact that helium does not burn. Although twice as heavy as hydrogen, helium has 92.6 per cent of the "lifting power" of hydrogen.

Neon, argon, krypton, and xenon are produced commercially by the fractional distillation or fractional liquefaction of air. Neon (and to some extent helium and argon) is used in the so-called *neon signs* so widely used in advertising, in airplane beacons, etc. Such signs may

be operated at low cost and penetrate fog much better than ordinary electric lights. The different colors produced depend upon the colors of the glass tubes used, the relative quantities of neon, argon, and helium employed, and the presence of mercury vapor and other foreign substances. Argon is used chiefly in filling electric light bulbs. Nitrogen was formerly used for this purpose, but the bulbs filled with argon are much more efficient, serve longer, and produce a light more like natural daylight. There are at present no large-scale uses for krypton and xenon because of their scarcity and high cost of production. There is, however, evidence that electric light bulbs filled with these two gases are even more efficient than those filled with argon.

THERMOCHEMISTRY

5.8. Forms of Energy

It has already been pointed out that every chemical reaction is accompanied by a characteristic energy change. Energy is usually defined as the ability of a body to perform work and is recognized in many different forms such as electrical energy, mechanical energy, chemical energy, kinetic energy, and potential energy. Kinetic energy is energy possessed by a body in motion and is equal to one-half the product of its mass and the square of its velocity,

$$\text{Kinetic energy (K.E.)} = \tfrac{1}{2}mv^2$$

Potential energy is energy that is possessed by a body by virtue of its position. Chemical energy is merely a special name for the kinetic and potential energies which are possessed by atoms and molecules and which become evident when these atoms and molecules undergo chemical change.

The law of conservation of energy holds that energy may be neither created nor destroyed. One form of energy may be converted into one or more other forms, but the total quantity of energy is thereby unchanged. Thus, the kinetic energy of a waterfall may be converted into electrical energy, heat energy may be converted to mechanical energy, etc.

5.9. Exothermal and Endothermal Reactions

The energy changes that accompany chemical reactions are usually expressed in terms of heat energy. Heat energy is measured in terms of a unit known as the *calorie*, which is the quantity of heat required to raise the temperature of one gram of water from 15° to 16°C. It is

frequently desired to incorporate in chemical equations information as to the number of calories of heat liberated or absorbed, and equations so written are usually called *thermochemical equations.* There is no sound basis for predicting whether heat will be liberated or absorbed in any given chemical reaction; this information must be obtained by experiment.

Chemical changes in which heat is given up to the surroundings (liberated) are known as *exothermal* reactions. Since heat is liberated, the heat may be considered as a product of the reaction and so represented in the thermochemical equation, thus,

$$C + O_2 \rightarrow CO_2 + 94{,}237 \text{ cal.}$$

This equation provides the information that the union of 12 g. of carbon (in the form of graphite) and 32 g. of oxygen results in the formation of 44 g. of carbon dioxide and the liberation of 94,237 cal. of heat. This quantity of heat is liberated regardless of whether the 12 g. of carbon is burned slowly or rapidly. Other examples of exothermal reactions are given by the equations

$$2H_2 + O_2 \rightarrow 2H_2O + 136{,}720 \text{ cal.}$$
$$S + O_2 \rightarrow SO_2 + 70{,}940 \text{ cal.}$$
$$4P + 5O_2 \rightarrow 2P_2O_5 + 739{,}800 \text{ cal.}$$
$$4Na + O_2 \rightarrow 2Na_2O + 200{,}520 \text{ cal.}$$
$$2KClO_3 \rightarrow 2KCl + 3O_2 + 26{,}260 \text{ cal.}$$
$$2PbO_2 \rightarrow 2PbO + O_2 + 75{,}400 \text{ cal.}$$

From experience in the laboratory the student may have learned that the decomposition of $KClO_3$ requires the application of heat and may wonder why this should be so in the case of an exothermal reaction. As pointed out in Sec. 5.2, the heat applied serves merely to raise the temperature to an extent such that the *rate* of the exothermal decomposition becomes appreciable.

If, on the other hand, heat is absorbed from the surroundings during a chemical change, the reaction is said to be an *endothermal* reaction. Since the heat energy in such a case is required for the occurrence of the reaction, the heat may be looked upon as one of the reactants and accordingly represented on the left of the arrow in the thermochemical equation,

$$2HgO + 43{,}200 \text{ cal.} \rightarrow 2Hg + O_2$$
$$2KNO_3 + 61{,}120 \text{ cal.} \rightarrow 2KNO_2 + O_2$$

These equations show that definite quantities of heat are absorbed in the decomposition of definite quantities of mercuric oxide and potassium nitrate. For no apparent good reason other than the fact that it has become conventional practice to do so, heat absorbed in endothermal reactions is most commonly represented to the right of the arrow in the thermochemical equation. Thus, the foregoing equations may be written in conventional form by transposition of the heat term to the right-hand side of the arrow (equality sign) with the necessary change in sign.

$$2HgO \rightarrow 2Hg + O_2 - 43{,}200 \text{ cal.}$$
$$2KNO_3 \rightarrow 2KNO_2 + O_2 - 61{,}120 \text{ cal.}$$

Hence, the *sign* of the heat term indicates whether the reaction is exothermal or endothermal.

Information concerning the quantity of heat energy involved in chemical reactions is important because **the tendency toward the occurrence of a chemical change is roughly proportional to the quantity of heat liberated.** Thus, if a large quantity of heat is liberated in a given reaction, the tendency for this reaction to occur is relatively great; if the quantity of heat liberated is small, the tendency for such a reaction to occur is correspondingly small.

5.10. Distinction between Heat and Temperature

Heat has been defined as a form of energy which may be measured in terms of calories. Hence, the use of the term *heat* carries the implication of *quantity*. Care should be exercised in order that the terms *heat* and *temperature* may not be confused. Suppose that two containers are filled with water and heated (supplied with calories) at the same rate until the water in the smaller container boils. If the same number of calories is supplied to the contents of both containers, the *temperature* of the boiling water in the smaller container is 100°C. while that of the water in the larger container is somewhat less than 100°. Although the same number of calories is transferred to both bodies of water, the heat supplied to the larger body of water is not sufficient to cause boiling because this heat is distributed throughout a larger volume of water. Thus, temperature is a measure of the extent to which calories are piled up on or within a body of matter or the extent to which these heat units are concentrated within a given volume. Heat, then, is a quantity factor, while temperature is an *intensity factor*.

5.11. Measurement of Temperature

Temperature is commonly (but not always) measured by an instrument called a *thermometer*, usually consisting of a glass bulb which is attached to a long glass tube having a small capillary bore and which is graduated in divisions called *degrees*. The glass bulb is filled with mercury or another liquid that expands when heated and rises in the

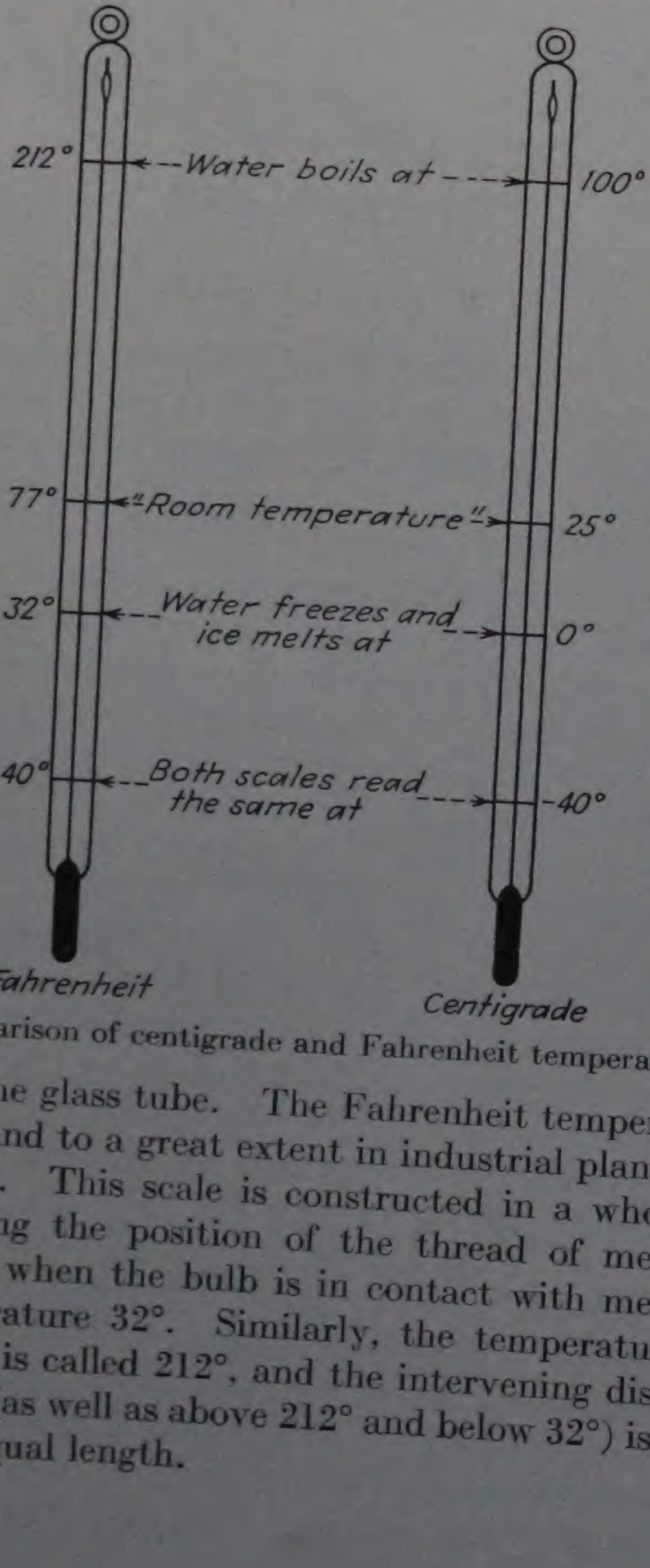

FIG. 31. Comparison of centigrade and Fahrenheit temperature scales.

small opening in the glass tube. The Fahrenheit temperature scale is used in the home and to a great extent in industrial plants in English-speaking countries. This scale is constructed in a wholly arbitrary manner by marking the position of the thread of mercury in the thermometer stem when the bulb is in contact with melting ice and calling this temperature 32°. Similarly, the temperature of boiling water on this scale is called 212°, and the intervening distance on the thermometer stem (as well as above 212° and below 32°) is divided into scale divisions of equal length.

The centigrade scale has been arbitrarily established in the same manner except that the temperature of melting ice is taken as 0° and the temperature of boiling water is called 100°. This scale is the one most commonly used in scientific work throughout the world. It is frequently necessary to convert temperature readings from one thermometer scale to another. A comparison of the Fahrenheit and centigrade scales (Fig. 31) provides a basis for such a conversion. Since each division on the Fahrenheit scale is five-ninths of one division on the centigrade scale, Fahrenheit temperatures may be converted to centigrade by the following relationship:

$$°C. = \tfrac{5}{9}(°F. - 32)$$

or

$$°F. = \tfrac{9}{5}(°C.) + 32$$

It should be understood clearly that both of these are arbitrary man-made temperature scales. Another scale which has its foundation in the natural behavior of matter is considered in the next chapter.

5.12. Temperature and Chemical Change

The occurrence of chemical reactions is believed to be dependent upon the ability of molecules to move through space as a result of their kinetic energy. If the temperature of a substance is increased (*i.e.*, if heat energy is supplied), the heat energy is converted to, and hence serves to increase, the kinetic energy of the molecules. Since the mass of the individual molecules does not change (K.E. = $\frac{1}{2}mv^2$), the velocity of their motion must be increased. Accordingly, an increase in temperature increases the kinetic energy of the molecules with a corresponding increase in the frequency of collisions, and therefore in the rate at which the molecules can undergo change.

Although not a hard and fast rule, the following is a very useful generalization with respect to the influence of temperature upon the rates of chemical reactions in general: *For reactions occurring at ordinary temperatures, the rate of reaction is approximately doubled by a temperature increase of* 10°*C.*

5.13. Other Factors That Influence the Rates of Chemical Reactions

In addition to temperature, two factors that influence the rates of chemical changes are (1) concentration and (2) catalysis. The influence of catalysts has already been discussed.

By the term *concentration* is meant the quantity of matter contained

in some definite volume. Concentration might be expressed in terms of the number of grams of a substance contained in a volume of 1 cc. or 1 liter. It might be useful also to express concentration in terms of the number of molecules or atoms of a substance contained in some unit of volume such as a cubic centimeter or a liter.

The manner in which the rate of a chemical reaction may be influenced by a change in concentration may be understood by considering one or two simple examples. If a wooden splint is heated in air (which contains about 21 per cent of oxygen) until the splint glows and then

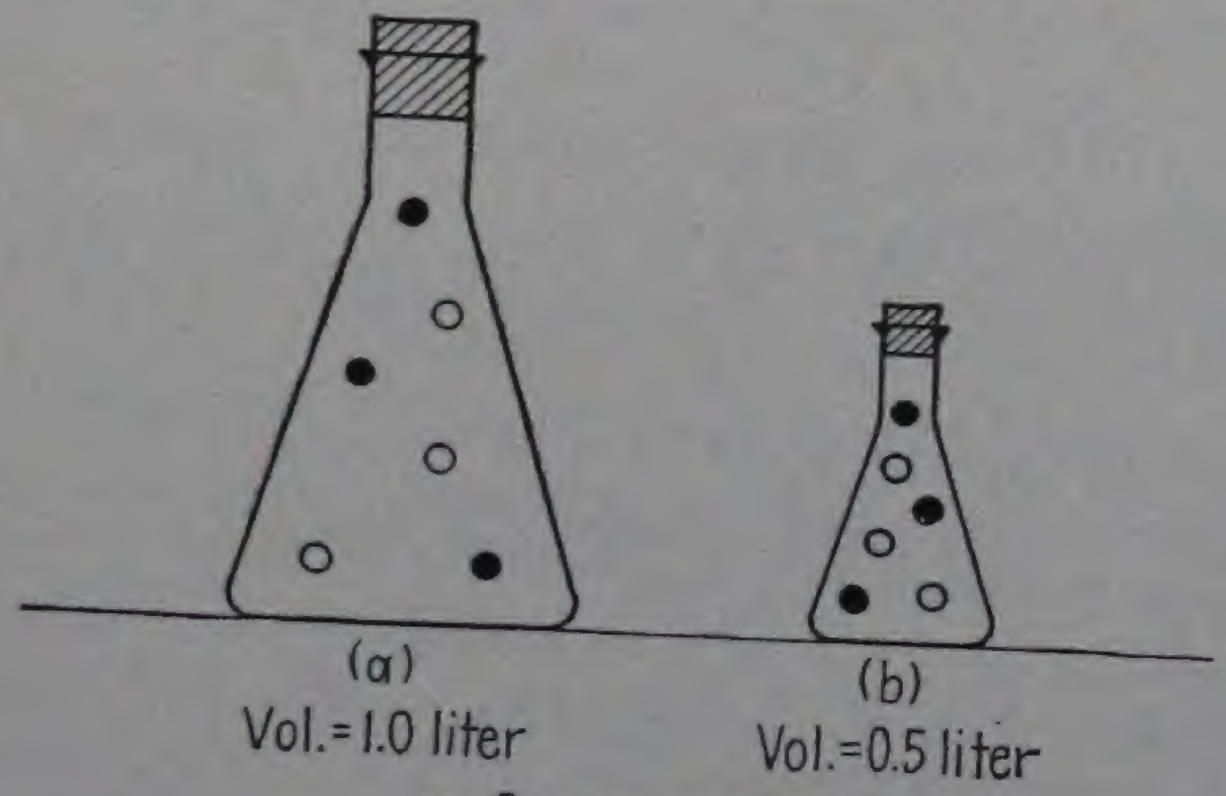

FIG. 32. Concentration of gas molecules.

is thrust into a test tube containing pure oxygen, the glowing splint bursts into flame. The reason for this is that the glowing splint has been brought into an atmosphere that is richer in oxygen than is ordinary air, *i.e.*, the concentration of oxygen is greater in the test tube and accordingly the union of the wood with oxygen proceeds at a greater rate. To consider another example, suppose that it is desired to produce nitric oxide by the direct union of nitrogen and oxygen.

$$N_2 + O_2 \rightarrow 2NO$$

If 3 molecules of nitrogen and 3 molecules of oxygen are mixed in a closed 1-liter flask (Fig. 32), the reaction proceeds at a definite rate which depends upon the temperature and upon the frequency with which the molecules collide as they move through space. If, now, the same number of molecules of nitrogen and oxygen is placed in a $\frac{1}{2}$-liter flask at the same temperature, the reaction proceeds more rapidly than in the first case because the concentration of the reacting substances has been increased. In the $\frac{1}{2}$-liter flask, the concentration (number of molecules per unit volume) is twice as great as in the 1-liter flask, and

the molecules of nitrogen and oxygen collide more frequently and therefore react more rapidly.

The rates of reaction of solid substances are also dependent upon their state of subdivision. A large compact lump of a solid material cannot, for example, react with oxygen so rapidly as would be the case if the large lump were first ground to a fine powder. A lump of coal is burned only slowly, but finely powdered coal may be caused to react with ordinary air at an explosive rate—a chemical change that is involved in many mine explosions. The more finely subdivided materials react at greater rates because so much more surface is exposed.

GENERAL EXERCISES

1. Define the following terms: (*a*) catalyst, (*b*) accelerator, (*c*) retarder, (*d*) combustion, (*e*) kinetic energy, (*f*) potential energy, (*g*) chemical energy, (*h*) concentration.

2. What are allotropic modifications of an element?

3. Distinguish between (*a*) positive and negative catalysis, (*b*) exothermal and endothermal reactions, (*c*) heat and temperature.

4. List three experimental conditions that influence the rates of chemical reactions.

5. Give important commercial uses for (*a*) oxygen, (*b*) helium, (*c*) neon, and (*d*) argon.

6. Explain the conditions necessary for the occurrence of spontaneous combustion.

7. What conclusion may be drawn from a knowledge of the quantity of heat liberated during a given chemical reaction?

8. If the decomposition of potassium chlorate is an exothermal reaction, why is it necessary to heat the compound when it is used in the laboratory preparation of oxygen?

9. How do laboratory methods for the production of elements and compounds differ from commercial methods?

10. At what temperature is the value on the centigrade scale identical with that on the Fahrenheit scale?

11. In what range of temperatures would it make little difference whether one expresses temperatures on the centigrade or Fahrenheit scale?

PROBLEMS

1. Convert the following centigrade temperatures to the corresponding Fahrenheit temperatures: (*a*) 86°C., (*b*) 327°C., (*c*) 438°C., (*d*) 1535°C., (*e*) 32°C., (*f*) 0°C., (*g*) −73°C.

2. Convert the following Fahrenheit temperatures to the corresponding centigrade temperatures: (*a*) 100°F., (*b*) −162°F., (*c*) 0°F., (*d*) 32°F., (*e*) 212°F.

3. "Room temperature" is usually considered to be 25°C. What is the corresponding Fahrenheit temperature?

4. Calculate the percentage of oxygen in (*a*) potassium chlorate, (*b*) manganese dioxide, (*c*) potassium nitrate, (*d*) lead dioxide, and (*e*) mercuric oxide.

5. Calculate the weight of oxygen which can be obtained by heating 100 lb. of each of the compounds listed in Prob. 4.

6. What weights of oxygen can be produced by heating (*a*) 1 g. of potassium chlorate, and (*b*) 1 g. of mercuric oxide?

7. If potassium chlorate costs 45 cents per pound, manganese dioxide costs 24 cents per pound, and potassium nitrate costs 34 cents per pound, which of these three substances is the cheapest source of oxygen if the cost of the oxygen compound is the only factor involved?

8. (*a*) How many pounds of oxygen are contained in 100 lb. of pure water? (*b*) What is the percentage of oxygen in water?

9. What quantity of heat is liberated during (*a*) the decomposition of 4.6 g. of potassium chlorate, (*b*) the burning of 16 g. of sulfur, (*c*) the production of 100 g. of PbO from PbO_2, and (*d*) the conversion of 0.05 g. of hydrogen to water by reaction with oxygen?

10. What quantity of heat is absorbed in (*a*) the decomposition of 85 g. of mercuric oxide, and (*b*) the production of 0.66 g. of oxygen from potassium nitrate?

11. If the decomposition of a sample of potassium nitrate absorbs exactly 100 cal. of heat, how many milligrams of oxygen are liberated at the same time?

SUGGESTED READING

Journal of Chemical Education

Meyer, Chromium Trioxide as a Catalyst in Potassium Chlorate Decomposition, **17**, 494 (1940).

Cunneen, Some Catalytic Reactions, **17**, 262 (1940).

Mitchell, Heterogeneous Catalysis, **9**, 261 (1932).

Alexander, Some Aspects of Catalysis, **9**, 2026 (1932).

Livingston, An Introduction to Chemical Catalysis in Heterogeneous Systems, **7**, 2887 (1930).

Hendrick, Catalysis—A New Factor in Industry, **2**, 631 (1925).

Carter and Heinrich, Modern Uses of Oxygen, **19**, 91 (1942).

Worsfold, On Ozone, **9**, 291 (1932).

Gibson, Rare Gases in Everyday Use, **18**, 533 (1941).

Seibel, Helium and Natural Gas, **3**, 45 (1926).

Bartlett, Accomplishing Much by Doing Nothing, **4**, 1376 (1927).

Brown, Some Early Thermometers, **11**, 448 (1934).

Barnett, A Brief History of Thermometry, **18**, 358 (1941).

Clewton, The Energy Factor in Chemical Changes, **8**, 683 (1931).

Industrial and Engineering Chemistry

Cady, Beginnings of the Helium Industry, **30**, 845 (1938).

Seibel, Production of Helium at Amarillo, **30**, 848 (1938).

Meyerhoff, Traces from Texas, **27**, 112 (1935).

CHAPTER 6

PROPERTIES OF GASES

Each of the three states of matter has certain characteristic properties which are different from those of the other two. Solids are relatively dense materials and retain their form regardless of the size or shape of the container in which they are placed (Fig. 33). Liquids have the ability to flow and to assume the shape of any vessel in all except the vertical direction. Gases differ from liquids and solids in that they enjoy relatively unrestricted motion and are capable of moving through space at high velocities and of distributing themselves uniformly in all directions throughout the vessel in which they are confined.

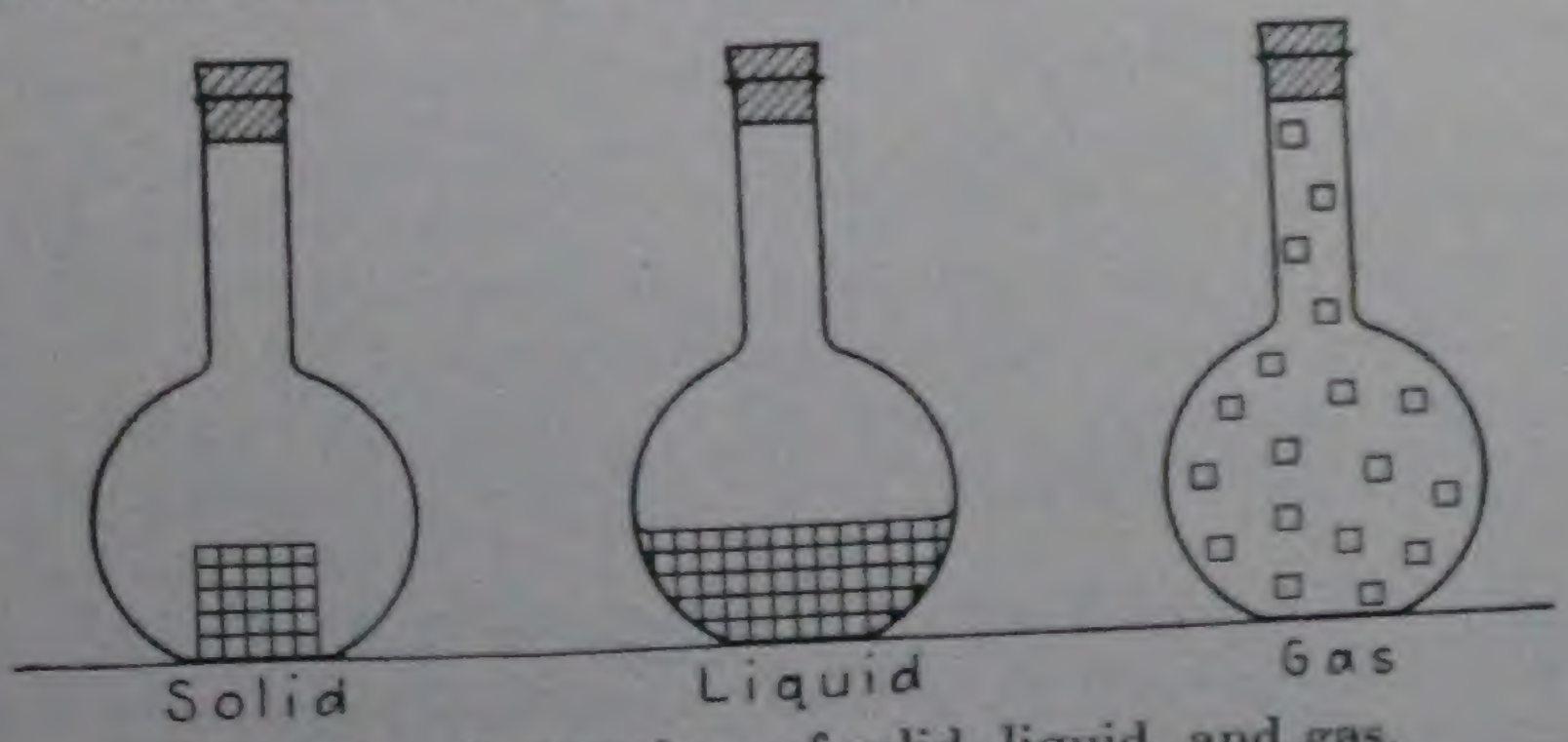

FIG. 33. Comparison of solid, liquid, and gas.

Although man lives in a gaseous atmosphere, he is less aware of the existence of gases than of the existence of liquids and solids. This is largely due to the fact that many of the most common gases are colorless, odorless, and of low density.

6.1. Regularities Observed in the Behavior of Gases

Progress in the understanding of chemical changes requires a knowledge of the make-up or structure of the various forms of matter. It has been known for a long time that the structure of gaseous substances is much simpler and more easily studied in the laboratory than the structure of either liquids or solids. Furthermore, much of the information gained from the study of gases is of value in attempts to learn of the structure of liquids and solids. Experiments performed by scientists over a long period of time have shown that all the common

gases behave very much (although not exactly) alike. For example, it is a familiar fact that confined gases exert pressure on the walls of their containers. All gases tend to expand when heated. These and other facts suggest that the structures of different gases must be very similar.

6.2. Kinetic-molecular Theory

In an effort to explain the behavior of matter in the gaseous condition, there has been developed a mental picture known as the *kinetic-molecular theory*. To understand this theory and to utilize it in the study of gases require the exercise of one's imagination. The principal ideas that make up the kinetic-molecular theory may be outlined as follows:

1. *A gas is believed to consist of molecules separated by relatively wide empty spaces.*

2. *The diameters of the gas molecules are very small in comparison with the distance between molecules.* These ideas are wholly reasonable in view of the low density of gases. If this were not the case, one could not walk through a gaseous atmosphere without encountering resistance similar to that met in walking through water.

3. *Gas molecules are in a constant state of rapid and chaotic motion.*

4. *Gas molecules move in straight lines until they collide with other molecules or with the walls of the containing vessel.* The sum of the impacts of billions of moving gas molecules against the walls of a closed container constitutes the *pressure* exerted by a confined gas. The walls of a vessel filled with a gas may be thought of as being constantly "bombarded" by rapidly moving molecules.

5. *When gas molecules collide, they rebound without loss of energy.* If this were not true, gas molecules would suffer a loss in kinetic energy upon collision and finally would be incapable of existing in the gaseous state. It is largely because of the "elastic" character of these collisions that gas molecules do not settle to the bottoms of their containers under the influence of gravity.

6. *The average kinetic energy of all different kinds of gas molecules is the same.* Since different kinds of gas molecules have different masses, their velocities must be such as to give all the same *average* kinetic energy (K.E. = $\frac{1}{2}mv^2$) at any specified temperature. This means simply that light molecules must have velocities of motion greater than those of heavy molecules.

7. *There exists between gas molecules a force of attraction which, at ordinary temperatures and pressures, is small in comparison with the*

kinetic energy. This force of attraction or cohesion is ordinarily so small that it is incapable of overcoming the influence of the kinetic energy which serves to keep the molecules apart and in motion.

At first glance, this theory may appear to be somewhat visionary, particularly in view of the fact that it is impossible to observe the behavior of any single molecule or any small number of molecules. Nevertheless, the more that is learned about the behavior of gases, the more sound does this theory appear to be. The ultimate test of any theory is the success attendant upon its use in the interpretation of the results of actual experiments.

6.3. Gas Laws

The study of gases has led to the formulation of a number of *laws* which serve to describe the behavior of substances in the gaseous condition. These laws may be stated either in words or in the form of exact mathematical expressions. It should be understood clearly that these are not man-made laws. They are simply concise descriptions of observed habits of nature; they *describe* but do not *govern*.

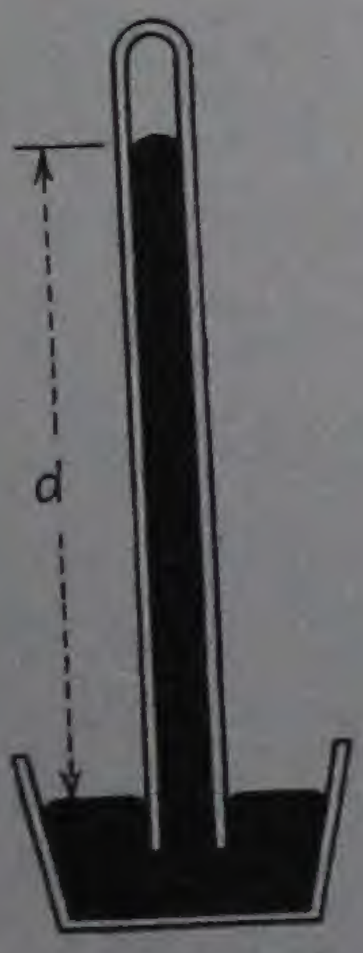

FIG. 34. A simple type of barometer.

6.4. Measurement of Pressure

A familiar example of the exertion of pressure by gases is the pressure of the atmosphere. It is well known that the pressure exerted by the gaseous atmosphere is less at the top of a mountain than at the bottom. The pressure exerted by the atmosphere (or any other gas) may be measured by an instrument known as the *barometer*, a simple form of which is shown in Fig. 34. A glass tube 800 mm. (about 31.5 in.) in length is closed at one end, filled with mercury, inverted, and the open end placed beneath the surface of mercury contained in an open vessel. The mercury falls in the tube, and a *vacuum* is formed above the mercury. The reason that all of the liquid mercury does not flow from the tube owing to gravitational attraction is that some is prevented from doing so by the pressure exerted by the atmosphere upon the surface of the mercury in the open vessel. The pressure exerted by the atmosphere is measured by the distance d between the level of the mercury in the tube and the level of the mercury in the open vessel. At sea level, the average pressure of the atmosphere is sufficient to support a column of mercury 760 mm. in height and is called *one atmosphere* (1 atm.). Accordingly, a pressure of 2 atm. would mean a

pressure equal to that exerted by a column of mercury 1520 mm. in height, or twice the average pressure of the atmosphere at sea level.

6.5. Measurement of Volume

The unit of weight known as the *gram* has already been defined as the weight of one milliliter of water at 4°C. Accordingly, one kilogram (1000 g.) of water at 4°C. represents the weight of one *liter* of water. For purposes of comparison it is convenient to remember that the liter is a unit of volume just a little larger than the quart, since 1 liter = 1.0567 qt. In scientific work, relatively large volumes of liquids or solutions are expressed in terms of liters while smaller volumes are expressed in terms of *milliliters*. One milliliter is one one-thousandth part of a liter. The term *milliliter* is abbreviated as ml.

Another unit of volume which is commonly used, particularly in dealing with gases, is the *cubic centimeter* (abbreviated, cc.). A cubic centimeter is the volume enclosed by a cube one centimeter on an edge (inside measurement). Since 1 liter (1000 ml.) = 1000.028 cc., the two units, milliliter and cubic centimeter, are not identical. Although the difference between the two is so small as to be negligible for most purposes, the milliliter is most commonly used in expressing small volumes of liquids and solutions, while the two are used interchangeably in work involving small volumes of gases.

6.6. Relation between Pressure and Volume; Boyle's Law

If a definite quantity of a gas is confined at some fixed temperature in a cylinder fitted with a movable piston, the position of the piston is such that the pressure exerted by the gas contained in the cylinder is the same as that exerted by the outside atmosphere (Fig. 35). If now the outside pressure is increased to 2 atm., the piston moves downward in the cylinder until the confined gas occupies essentially one-half of the original volume. That is, if the pressure is doubled, the volume is decreased by one-half. Experiments of this kind led Robert Boyle, in the year 1660, to state what has come to be known as *Boyle's law:* **At constant temperature, the volume occupied by a definite weight of gas is inversely proportional to the pressure.** Or,

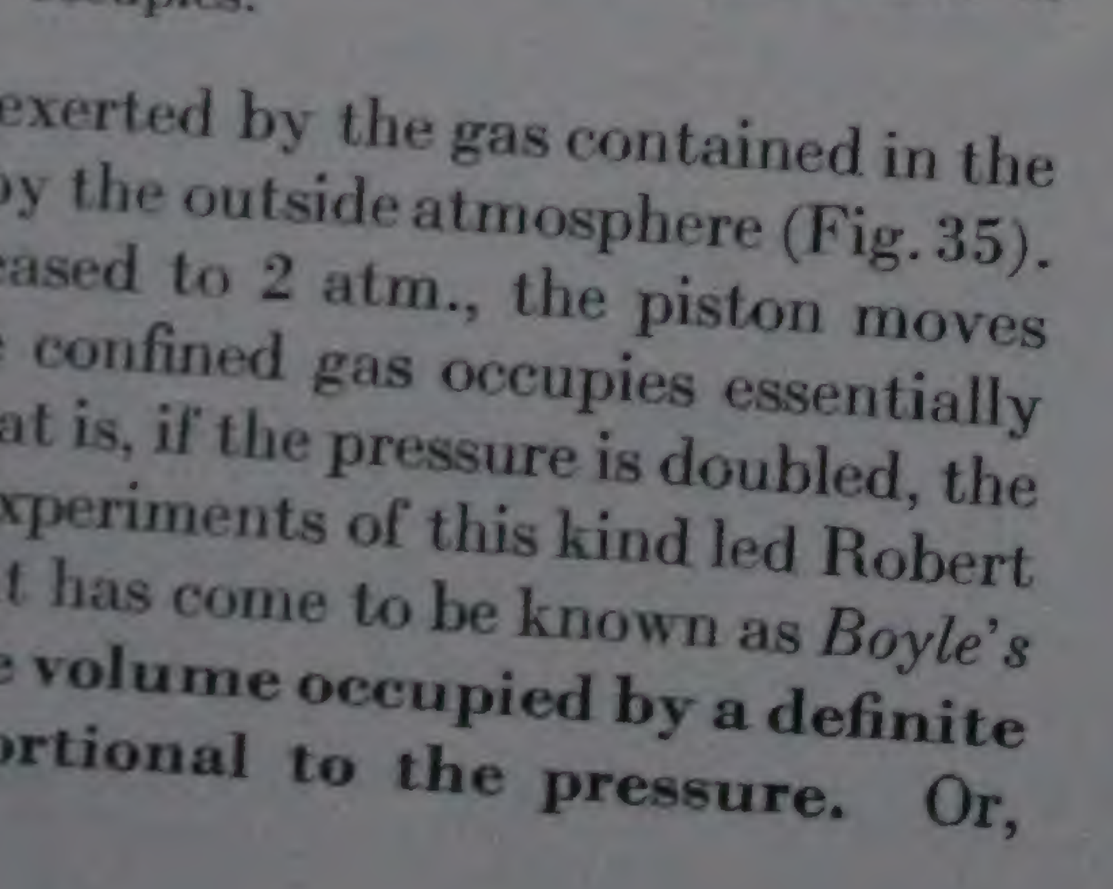

FIG. 35. The relationship between the pressure exerted upon (or by) a confined gas and the volume which it occupies.

stated in the form of a mathematical expression,

$$v \propto \frac{1}{p}$$

where v represents the volume and p represents the pressure. An *inverse* relationship such as this requires that, if one of two factors changes in a given direction (*e.g.*, increases), the other factor must change to the same extent but in the opposite direction (*i.e.*, must decrease).

To replace the proportionality sign by an equality sign requires the introduction of a proportionality constant, k,

$$v = k\frac{1}{p}$$

or

$$pv = k$$

which is the usual mathematical expression of Boyle's law.

By reference to Fig. 35, Boyle's law may be explained in terms of the kinetic-molecular theory. In the first cylinder, the pressure exerted on the inner surface of the piston is the result of bombardment by the moving gas molecules contained in the cylinder and is the same as the pressure being exerted (in the same manner) by gas molecules of the atmosphere. When the external pressure is doubled and the piston assumes position B, the pressure exerted by the confined gas molecules must also be equal to 2 atm. The original number of gas molecules has been crowded into half the original space. Accordingly, the number of molecules per unit of volume has been doubled, the number of collisions per unit of time is doubled, and this results in a pressure twice as great as the original pressure.

Application of Boyle's Law. Suppose that some definite weight of oxygen gas occupies a volume of 593 cc. when under a pressure of 710 mm. at 25°C. In certain practical problems, it might be required to know the volume that this weight of gas would occupy if the pressure was changed to 790 mm. and the temperature held constant. The answer to such a problem may be had readily by the application of Boyle's law. The volume v_2 under the new conditions of pressure is equal to the original volume v_1 multiplied by a suitable fraction.

$$v_2 = v_1 \times \text{(a fraction)}$$

This fraction may be looked upon as a correction factor which takes into account the change in pressure from $p_1 = 710$ mm. to the new

pressure $p_2 = 790$ mm. The next question that arises is whether the fraction should be $^{710}/_{790}$ or $^{790}/_{710}$. To decide on this point requires only that one recall that, according to Boyle's law, an increase in pressure must result in a decrease in volume. Since it is proposed to *increase* the pressure from 710 to 790 mm., the new volume v_2 must be less than the original volume v_1, and the fraction used as the correction factor must be $^{710}/_{790}$.

$$\begin{aligned} v_2 &= v_1 \times {}^{710}/_{790} \\ &= 593 \times {}^{710}/_{790} \\ &= 533 \text{ cc.} \end{aligned}$$

Other problems involving the application of Boyle's law are given at the end of this chapter.

6.7. Relation between Volume and Temperature

When a gas is heated in a closed container so that the volume cannot change, the pressure exerted by the gas increases until the walls of the container are ruptured. If an overinflated automobile tire is driven over a hot highway, indisputable evidence of this increase in pressure may be experienced. There arises the question, however, as to how the volume of a gas changes with change in temperature if the gas is allowed to expand against a constant pressure. It has been found that for each degree change in the centigrade temperature, there is a change in volume equal to $^1/_{273}$ of the volume at 0°C.

Absolute Temperature Scale. If some definite weight of a gas such as oxygen occupies a volume of 273 cc. at 0° under a pressure of 1 atm. and the temperature is lowered to −1°C., the volume occupied by the gas at −1°C. would be 272 cc. (*i.e.*, a decrease in volume of $^1/_{273}$ of the volume at 0°C.). With repeated lowering of the temperature, the volume decreases in this same regular fashion as is shown by the following data:

When $t = 0$°C.,	$v = 273$ cc.
When $t = -1$°C.,	$v = 272$ cc.
When $t = -2$°C.,	$v = 271$ cc.
When $t = -50$°C.,	$v = 223$ cc.
When $t = -150$°C.,	$v = 123$ cc.
When $t = -200$°C.,	$v = 73$ cc.
When $t = -273$°C.,	$v = ?$

It appears from the above data that, if the temperature were lowered to −273°C., the volume would be *zero* and the gas would have disap-

peared. This, of course, could not occur (law of indestructibility of matter). Before such a temperature as −273°C. could be reached, the oxygen would become a liquid and then pass into the solid state. The temperature of −273°C. is known as the *absolute zero* since it is that temperature at which the volume occupied by a gas should, theoretically, become zero if gases were capable of existence at such a temperature.

The absolute (or Kelvin) temperature scale is based upon the absolute zero and is related to the centigrade scale as follows:

$$°\text{A.} = °\text{C.} + 273$$

To convert centigrade temperatures to the absolute scale, it is necessary only to add 273 to the centigrade temperature. It should be emphasized that the absolute temperature scale is not an arbitrary one; rather it is one that is directly based on the manner in which the volume of a gas varies with the change in temperature at constant pressure.

Charles' Law. An examination of the preceding data reveals that the volume occupied by a gas changes in a regular manner when the temperature is changed. Essentially the same regularity would have been observed had the temperature been increased rather than decreased and had some gas other than oxygen been used. This change in volume with change in temperature is described by Charles' law, which was first stated in 1801: **At constant pressure, the volume occupied by a definite weight of gas is directly proportional to the absolute temperature.** Since a direct proportionality is involved, if the temperature is doubled, the volume is also doubled; if the temperature is halved, the volume must also be decreased to one-half the original volume. Stated mathematically, Charles' law becomes

$$v \propto t$$

and

$$v = kt$$

or

$$\frac{v}{t} = k$$

In terms of the kinetic-molecular theory, the pressure exerted by a gas depends upon the kinetic energy possessed by the molecules. If the temperature is increased, there is a corresponding increase in the kinetic energy of the gas molecules. As a result, they must move at greater velocities and consequently must strike exposed surfaces more frequently and with greater force. The gas expands against a con-

stant pressure and occupies a volume which is related (by Charles' law) to the extent of the temperature increase.

Application of Charles' Law. If a given weight of oxygen gas occupies a volume of 616 cc. at a temperature of 25°C. and under a pressure of 750 mm., the extent to which the volume changes if the temperature is lowered to 10°C. and the pressure is not permitted to change may be calculated as follows. The volume v_2 at the new temperature is equal to the original volume v_1 multiplied by a suitable fractional correction factor.

$$v_2 = v_1 \times (\text{a fraction})$$

The correction factor, in fractional form, is concerned only with the two *absolute* temperatures $t_1 = 25°\text{C.} + 273 = 298°\text{A.}$ and $t_2 = 10°\text{C.} + 273 = 283°\text{A.}$ According to Charles' law, if the temperature is *decreased*, the volume must also decrease, and v_2, therefore, is less than v_1. Accordingly, the fraction must be such that it represents a number less than unity, *i.e.*, $^{283}/_{298}$, and

$$\begin{aligned} v_2 &= v_1 \times {}^{283}/_{298} \\ &= 616 \times {}^{283}/_{298} \\ &= 585 \text{ cc.} \end{aligned}$$

6.8. Dalton's Law of Partial Pressures

Many experiments with gases are concerned with mixtures of different kinds of gases rather than with single pure gaseous substances.

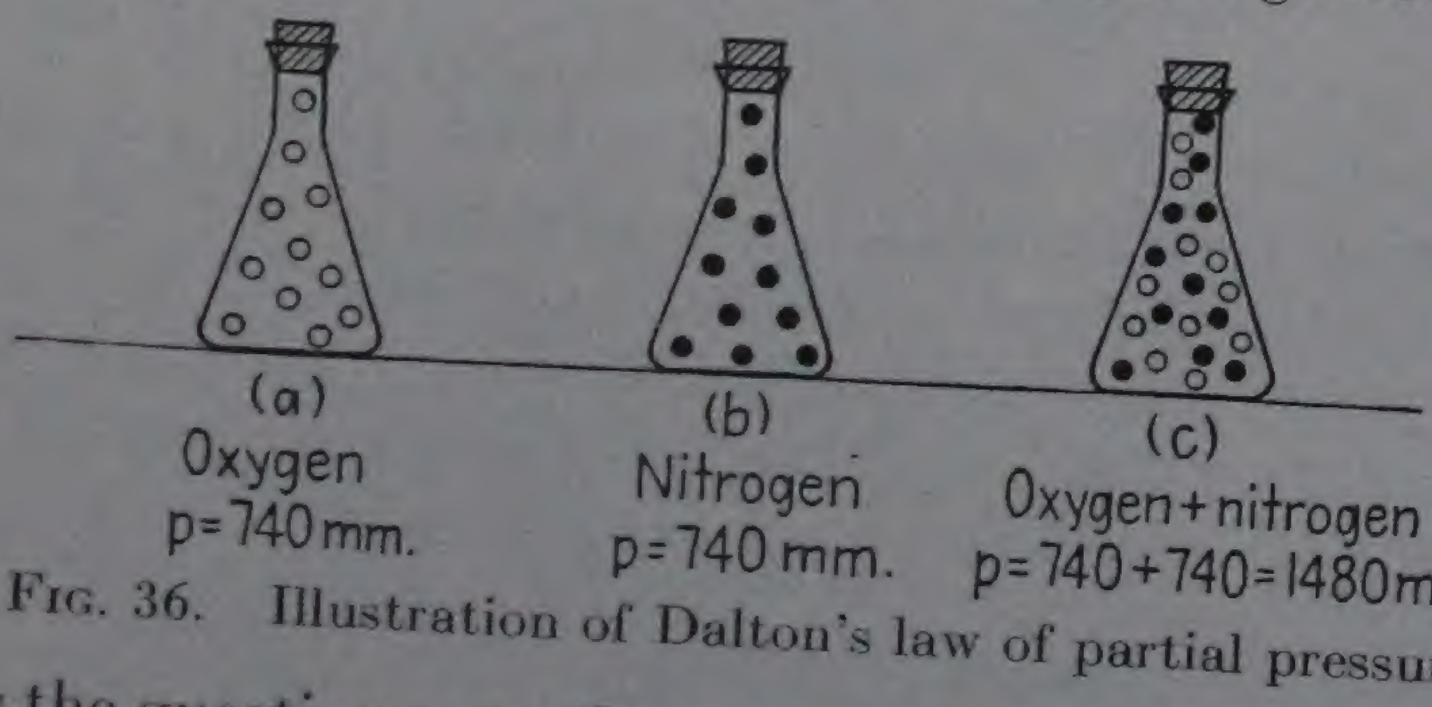

FIG. 36. Illustration of Dalton's law of partial pressures.

This raises the question as to the manner in which each gas in a mixture contributes to the total pressure exerted by the mixture. Suppose that a sample of pure oxygen gas is placed in a 1-liter flask (Fig. 36*a*) and exerts a pressure of 740 mm. and that a sample of pure nitrogen gas in a 1-liter flask also exerts a pressure of 740 mm. (Fig. 36*b*). If, now, the oxygen gas is forced into the flask containing the nitrogen (or vice versa) so that the two gases now occupy a total volume of 1

liter (Fig. 36*c*), the total pressure is found to be 1480 mm. (*i.e.*, 740 + 740 mm.). In other words, each gas in the mixture behaves just as though it were alone in the 1-liter flask and occupying the total volume of 1 liter. That part of the total pressure which is exerted by a given gas in a mixture is known as the *partial pressure* of that gas. The relation between total and partial pressures is described by Dalton's law: **The total pressure exerted by a mixture of gases is equal to the sum of the partial pressures of the various components.**

$$P_{(total)} = p_a + p_b + p_c + \cdots$$

where p_a, p_b, p_c, etc., are the partial pressures of the different gases in the mixture.

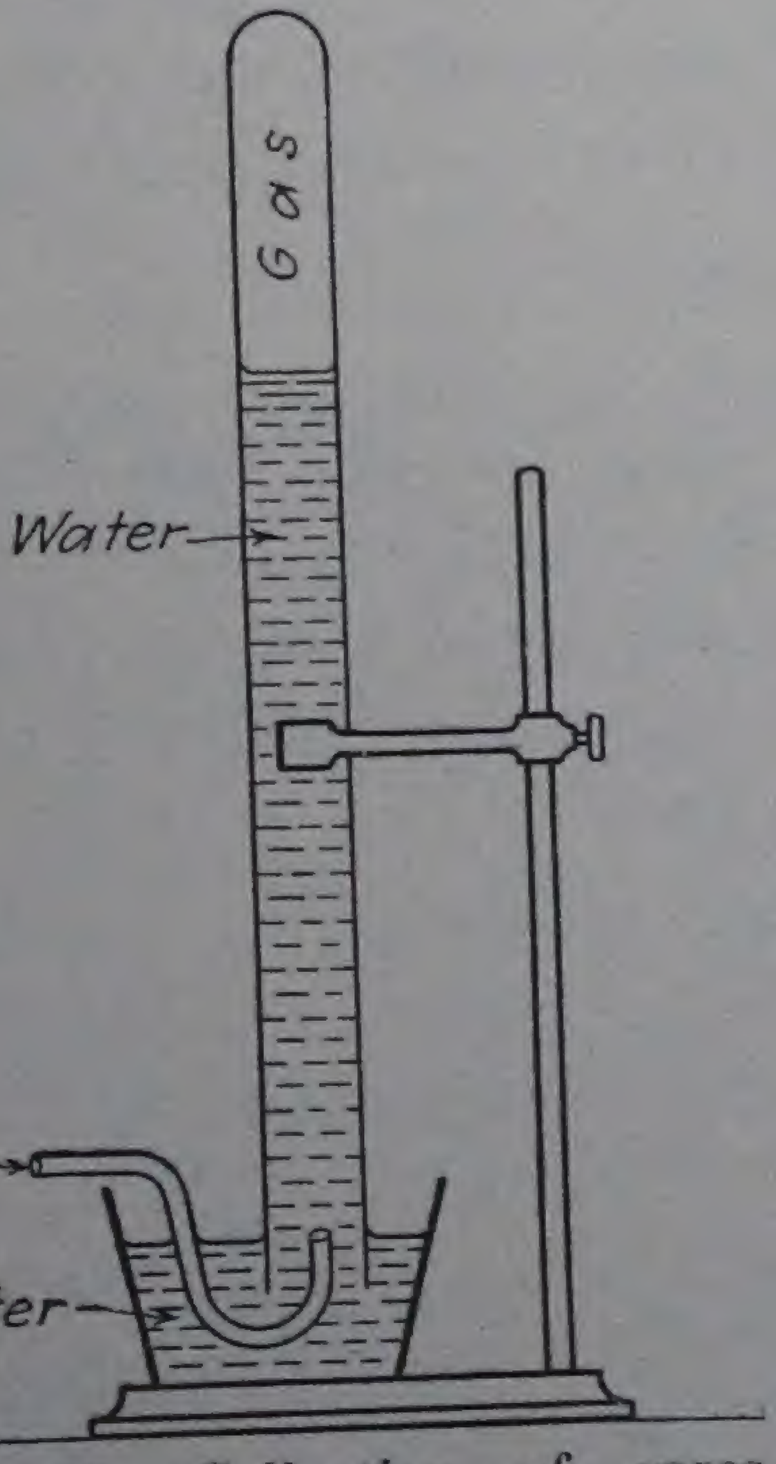

FIG. 37. Collection of gases over water.

6.9. Standard Conditions of Temperature and Pressure

From the foregoing discussion it is apparent that the volume occupied by a definite weight of gas has no real meaning unless the temperature and pressure are specified. In order to have a basis for the comparison of results of experiments which involve gases and which are conducted under different conditions of temperature and pressure, scientists have agreed to express gas volumes in terms of a *standard* set of conditions. The conditions agreed upon are a temperature of 0°C. (the melting temperature of ice) and a pressure of 760 mm. (the average pressure of the atmosphere at sea level). These are known as *standard conditions of temperature and pressure* and are commonly abbreviated S.T.P.

6.10. Experimental Measurement of Gas Volumes

In the laboratory, the volumes occupied by gases are usually measured by collecting and confining the gases over mercury, water, or some other suitable liquid. If a gas such as oxygen is collected over water (Fig. 37), the gas in the tube consists of a mixture of oxygen and water vapor. The total volume of the mixture of gases contained in the tube may be read directly from the scale (usually in cubic centimeters) on the calibrated tube. When the level of the liquid in the open container

is the same as that of the liquid in the tube, the pressure exerted by the confined gas may be known simply by reading the barometer.

With the method illustrated by Fig. 37, 45 cc. of gas (oxygen + water vapor) was collected in a laboratory in which the temperature was 28°C. and the barometric pressure was 730 mm. The usual question that arises is, what volume would the *dry* oxygen gas occupy under standard conditions?

First, the total pressure P is, by Dalton's law, equal to the sum of the partial pressures of oxygen and water vapor.

$$p_{O_2} + p_{H_2O} = P_{(total)}$$
$$p_{O_2} = P_{(total)} - p_{H_2O}$$

In order to calculate the partial pressure of oxygen, it is necessary to know the partial pressure of water vapor. This information may always be obtained by referring to tables in which values for the vapor pressure[1] of water at different temperatures are listed as found by experiment (see Appendix). At 28°C., the partial pressure of water vapor is 28.3 mm.; hence,

$$p_{O_2} = P_{(total)} - 28.3$$
$$= 730 - 28.3$$

The volume under standard conditions, $V_{S.T.P.}$, is equal to the measured volume after correction for the change in absolute temperature and the change in pressure.

$$V_{S.T.P.} = 45 \times \frac{730 - 28.3}{760} \times \frac{0° + 273}{28° + 273}$$
$$= 37.7 \text{ cc.}$$

In this case, the fractional correction factors are set up from the same line of reasoning as was used in solving the problems used to illustrate separately the application of the laws of Boyle and Charles.

6.11. Diffusion of Gases

All our ideas concerning the nature of gases are based upon the assumption that gases consist of molecules in motion. That molecules do move (diffuse) through space can be demonstrated by numerous simple experiments. If two flasks, one containing oxygen and the other containing hydrogen, are placed mouth to mouth as shown in Fig. 38*a* and allowed to remain in this position, the molecules of hydrogen move into the flask containing oxygen and the molecules of oxygen

[1] See Sec. 7.5.

move into the flask that originally contained only hydrogen (Fig. 38*b*). After sufficient time has elapsed, the two gases are found to be uniformly distributed throughout the two flasks, as shown in Fig. 38*c*.

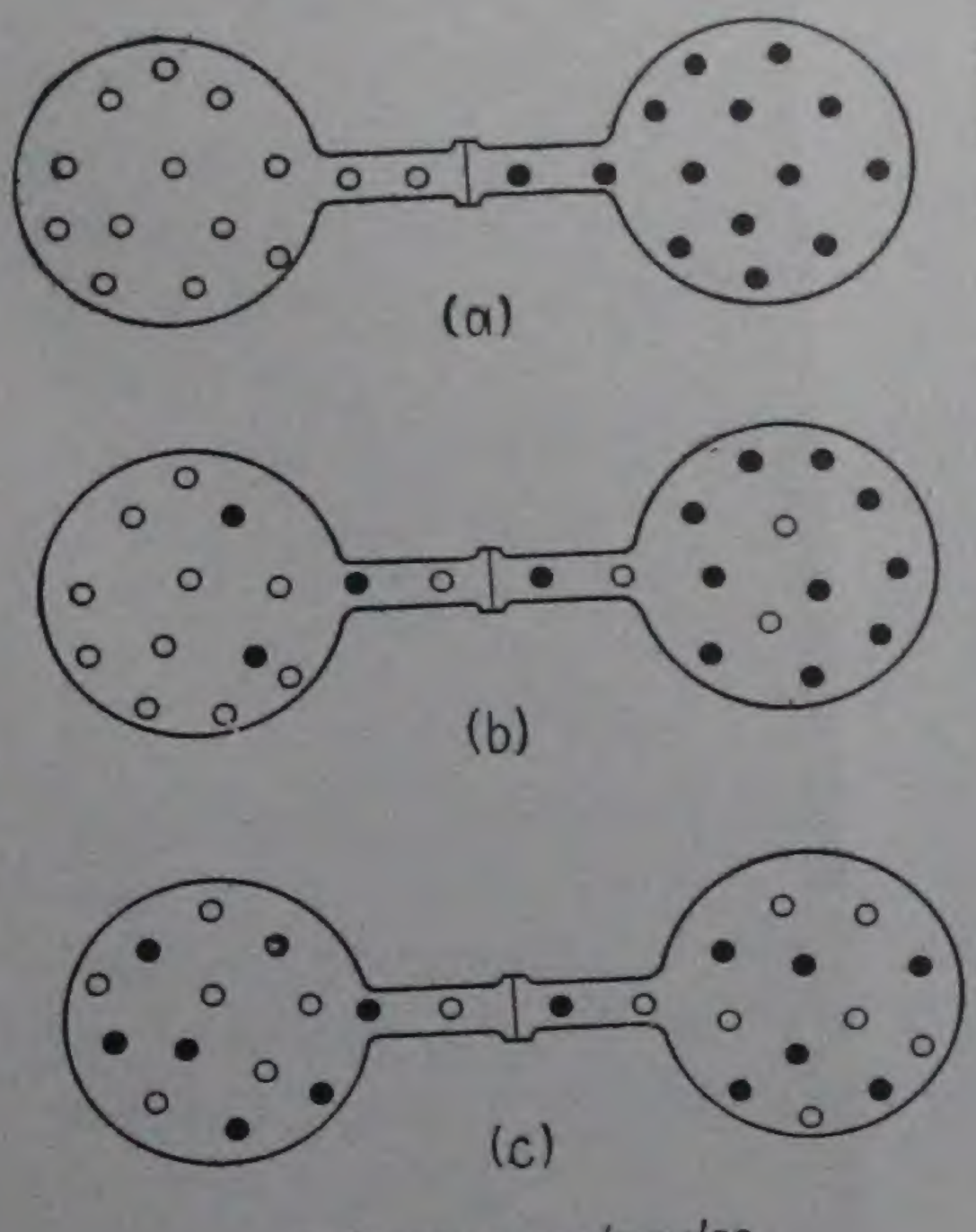

FIG. 38. Illustration of diffusion of gases.

Density of Gases. Density is defined as the weight of matter contained in a specified unit of volume. The density of a gas must, of course, be specified in terms of the temperature and pressure (usually standard conditions). The units in which density is expressed may be grams per cubic centimeter, pounds per gallon, or any other convenient units. The densities of a few common gases are listed in Table 6.

The density values in Table 6 are *absolute* values. Chemists sometimes prefer to use *relative* density, which is the ratio of the weight of a given volume of a gas to the weight of an equal volume of air (arbitrarily chosen as a convenient standard).

TABLE 6

ABSOLUTE DENSITY OF COMMON GASES UNDER STANDARD CONDITIONS

Gas	Density, g. per liter
Hydrogen	0.0899
Oxygen	1.4290
Nitrogen	1.2505
Hydrogen chloride	1.6392
Ammonia	0.7710
Air	1.2930

The relative density of hydrogen, for example, may be calculated as follows:

$$\text{Relative density of } H_2 = \frac{\text{absolute density of } H_2}{\text{absolute density of air}}$$

$$= \frac{0.0899}{1.2930}$$

$$= 0.0696$$

The relative densities of the gases listed in Table 6 are given in Table 7. Density should not be confused with *specific gravity*, which is defined as the ratio of the weight of a given volume of a substance to the weight of an equal volume of water at the same temperature (usually 4°C. the temperature at which water exhibits its maximum density).

TABLE 7

RELATIVE DENSITY OF COMMON GASES UNDER STANDARD CONDITIONS

Gas	Relative Density
Hydrogen	0.0696
Oxygen	1.1053
Nitrogen	0.9671
Hydrogen chloride	1.2677
Ammonia	0.5963
Air	1.0000

Rates of Diffusion; Graham's Law. If a heavy automobile and a light automobile were powered by the same kind of motor, the light car would, of course, be capable of traveling at the greater speed. Similarly, light molecules are capable of diffusing more rapidly than heavier molecules since the average kinetic energy of all kinds of gas molecules is the same. In 1832, Graham formulated a law to the effect that **the rate of diffusion of a gas is inversely proportional to the square root of its density.** If r represents the rate of diffusion and d represents the density, then,

$$r \propto \frac{1}{\sqrt{d}}$$

and

$$r = k\frac{1}{\sqrt{d}}$$

or

$$r\sqrt{d} = k$$

To provide some idea as to the absolute rate at which gas molecules move, it is of interest to note that hydrogen molecules (at ordinary temperatures) move at a rate of 1.14 *miles per sec.*

Usually, chemists are interested not so much in the absolute rate at which a given gas diffuses but rather in the relation between the rates of diffusion of two or more gases. In comparing, for example, the relative rates of diffusion of hydrogen and oxygen,

$$r_{H_2}\sqrt{d_{H_2}} = r_{O_2}\sqrt{d_{O_2}}$$

or

$$\frac{r_{H_2}}{r_{O_2}} = \frac{\sqrt{d_{O_2}}}{\sqrt{d_{H_2}}}$$

Since oxygen is sixteen times as heavy as hydrogen (1.4290/0.0899),

$$\frac{r_{H_2}}{r_{O_2}} = \frac{\sqrt{16}}{\sqrt{1}} = \frac{4}{1}$$

This means that, at the same temperature, hydrogen molecules diffuse four times as rapidly as oxygen molecules.

Demonstration of Rates of Diffusion. That hydrogen diffuses much more rapidly than ordinary air may be shown using an apparatus of the type shown in Fig. 39. *A* is a porous-walled porcelain cup containing air and connected by means of a glass tube to a bottle containing water. When the porous cup is surrounded by a bell jar filled with hydrogen, the hydrogen diffuses into the porous cup more rapidly than the air (oxygen and nitrogen) can diffuse out of the cup. This results in a positive pressure within the cup, and, as a result, the water is forced out of the bottle *B* through the glass outlet tube.

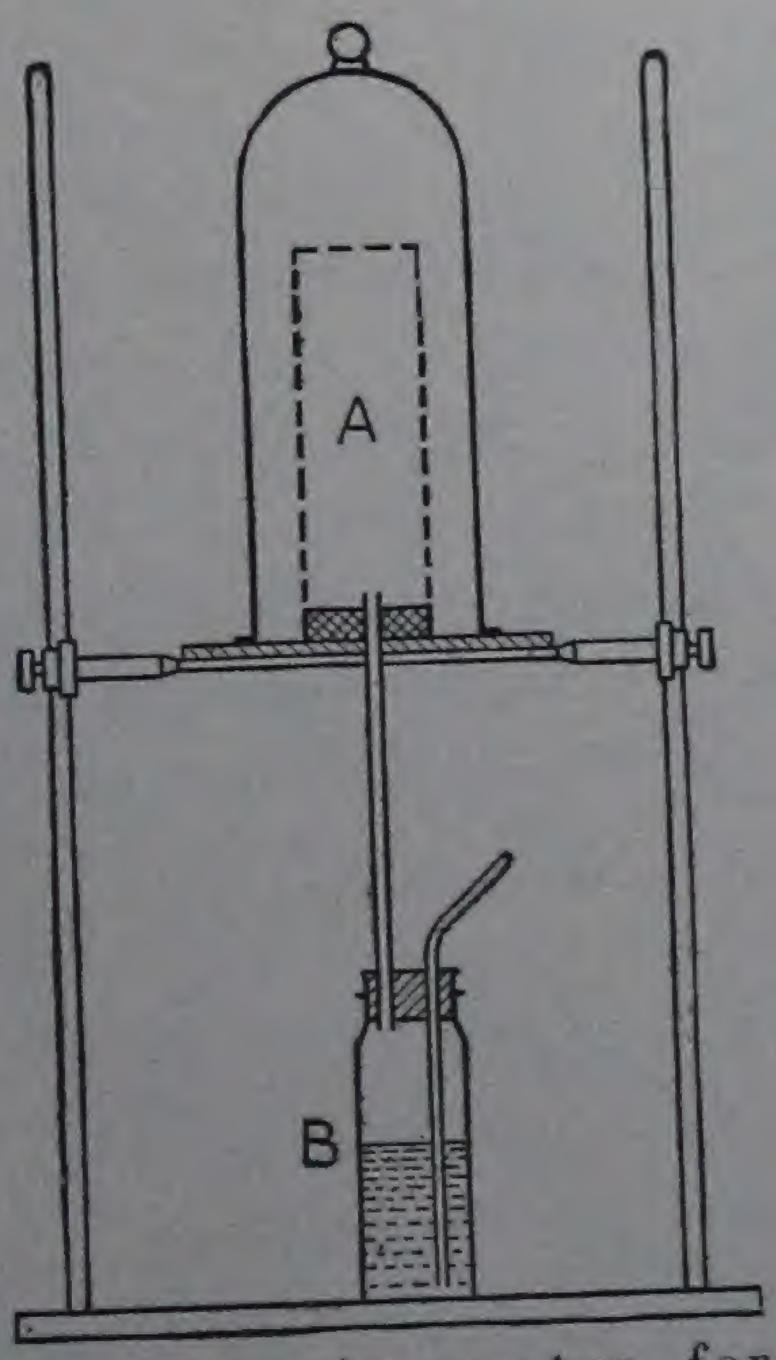

FIG. 39. Apparatus for demonstration of diffusion of gases.

6.12. The Ideal Gas

No real gas such as oxygen or hydrogen behaves *strictly* in accordance with the mathematically exact gas laws. In their behavior toward changes in temperature and pressure, real gases deviate slightly from the gas laws. When the pressure on a given volume of oxygen is doubled, the volume is decreased almost but not quite exactly one-half. Chemists study the behavior of gases in terms of an imaginary *ideal gas* which, if such existed, would behave precisely as described by the laws of Boyle, Charles, etc. Real gases deviate from the gas laws at ordinary pressures because of the forces of attraction between molecules; these forces would be absent in the ideal gas. At very low pressures the gas molecules are farther apart, the forces of attraction are relatively less effective, and the behavior of the real gas approaches

that of the ideal or perfect gas. However, this approach to ideal-gas behavior is realized only at very low pressures.

GENERAL EXERCISES

1. Define the following terms: (*a*) barometer, (*b*) density, (*c*) absolute zero, (*d*) partial pressure, (*e*) relative density, (*f*) ideal gas.

2. Outline the essential ideas involved in the kinetic-molecular theory.

3. State each of the following laws in words and in the form of exact mathematical expressions: (*a*) Boyle's law, (*b*) Graham's law, (*c*) Dalton's law, (*d*) Charles' law.

4. Suggest practical situations in which a knowledge of the relative density of a gas would be of importance.

5. Under what conditions could one raise the temperature of a given quantity of a gas without a corresponding increase in the volume occupied by the gas?

PROBLEMS

1. Convert the following temperatures to the corresponding values on the absolute scale: (*a*) 366°C., (*b*) −1°C., (*c*) 100°C., (*d*) −254°C., (*e*) −117°C., (*f*) 74°C., (*g*) 68°F., (*h*) −8°F.

2. Given the information that the absolute density of sulfur dioxide is 2.9269 g. per liter, calculate the density of this gas relative to air.

3. Calculate the relative density of (*a*) nitrogen toward air, (*b*) oxygen toward air, (*c*) ammonia toward air, (*d*) hydrogen chloride toward air, (*e*) oxygen toward hydrogen.

4. At a certain temperature, a sample of carbon dioxide gas occupies a volume of 871.3 cc. when under a pressure of 3 atm. If the temperature remains the same, what volume will the gas occupy if the pressure is decreased to 332 mm.?

5. When subjected to a pressure of 4263 mm. at 0°C., a certain quantity of helium gas occupies a volume of 3 cc. What pressure would be required to cause the same quantity of helium to occupy a volume of 1250 cc. at 0°C.?

6. A sample of gas occupies a volume of 5 cc. at 27°C. and 750 mm. What volume will this gas occupy at −3°C. and 800 mm.?

7. If a sample of gas occupies a volume of 100 liters at 15°C. and 750 mm., what volume will it occupy at S.T.P.?

8. If there is no change in pressure, by how much will the volume of 1.2 liters of gas at 27°C. be increased by raising the temperature to 127°C.?

9. A known weight of a gas occupies a volume of 700 cc. at 25°C. under atmospheric pressure. Calculate the volume occupied by the same weight of the gas under atmospheric pressure at 5000°C.

10. The volume occupied by a sample of nitrogen at 100°C. and 732 mm. is 510 liters. What volume will this gas occupy at a temperature of 273°A., if the pressure is held constant?

11. If a sample of gas occupies a volume of 10 cc. at S.T.P., what volume will it occupy at 273°C. when under a pressure of 5 atm.?

12. At 27°C. and 600 mm., a quantity of gas occupies a certain known volume. What pressure (in atmospheres) must be applied in order to prevent a change in volume when the temperature is increased 100°C.?

13. When collected over water in a laboratory in which the temperature was 30°C. and the barometric pressure was 695 mm., the gas obtained by heating some mercuric oxide occupied a volume of 82 cc. Calculate the volume of dry oxygen under standard conditions of temperature and pressure.

14. A sample of hydrogen was collected over water at 27°C. and 722 mm. and found to occupy a volume of 106 cc. Upon standing overnight, the temperature changed to 22°C. and the pressure increased to 753 mm. What volume did the wet gas occupy under these latter conditions?

15. A mixture of gases consists of nitrogen, oxygen, and argon and exerts a total pressure of 1.5 atm. If the partial pressure of oxygen is 427 mm. and the partial pressure of nitrogen is 531 mm., what is the partial pressure of argon, in millimeters?

16. A sample of air confined over water at 30°C. exerts a total pressure of 740 mm. What part of this pressure is due to dry air?

17. (*a*) Three hundred twelve liters of ammonia gas were confined over mercury at 0°C. and 607 mm. pressure. If the partial pressure of mercury vapor is considered to be negligible, what volume will this gas occupy at S.T.P.? (*b*) Calculate the weight of the ammonia, in grams.

18. A gas collected over water at 25°C. and 770 mm. occupies a volume of 300 cc. What is the corresponding volume of dry gas at S.T.P.?

19. What volume would 11.2 liters of dry oxygen at S.T.P. occupy if it were confined over water and saturated with water vapor in a laboratory in which the temperature is 20°C. and the barometric pressure is 755 mm.?

20. What weight of hydrogen (in grams) would be required to fill a 10-liter flask at −15°C. and 740 mm. pressure?

21. By application of Graham's law, show (*a*) that ammonia diffuses 1.29 times as fast as air, (*b*) that nitrogen diffuses 1.07 times as fast as oxygen.

SUGGESTED READING

Journal of Chemical Education

Clark, The Kinetic Theory, **1**, 75 (1924).

Timm, The Kinetic-molecular Theory and Its Relation to Heat Phenomena, **12**, 31 (1935).

Hays and Gustavson, Simple Apparatus for Demonstrating Boyle's Law, **16**, 115 (1939).

Wolthius, The Lowest Temperatures, **13**, 172 (1936).

Rosenblum, Upper Limit of Temperature, **17**, 438 (1940).

Meyer, The Solution of Gas Law Problems, **21**, 31 (1944).

CHAPTER 7

LIQUEFACTION OF GASES; PROPERTIES OF LIQUIDS AND SOLIDS

The relative simplicity of the structure of gases is due largely to the fact that gas molecules are normally so far apart that the forces of attraction between molecules cannot operate effectively against the kinetic energy that opposes these attractive forces. It is of interest, therefore, to inquire as to the changes that occur when the kinetic energy of gas molecules is decreased sufficiently to permit the attractive forces to assume a predominant role and to see whether the kinetic-molecular theory may be useful in explaining the nature of liquids and solids.

7.1. Liquefaction of Gases

In order to change a substance from the gaseous to the liquid state, it is necessary that the gas molecules be brought so close together that the attractive force between them can operate to hold them in close proximity in the condition that is recognized as the liquid state. This may be accomplished by either of two methods, (*a*) by lowering the temperature, (*b*) by increasing the pressure, or by a combination of these two methods.

When the pressure is held constant and the temperature is progressively lowered, the kinetic energy of the gas molecules becomes less and less. Under these conditions, the volume decreases and the molecules move with diminished velocity and through shorter distances; the gas molecules are brought closer and closer together. If the gas is cooled sufficiently, the kinetic energy becomes so small that the force of attraction is capable of holding the molecules in clusters, which first become visible in the form of a mist or fog. As these clusters of molecules become larger, drops of liquid appear. In this manner, any gas may be caused to pass from the gaseous to the liquid condition.

The molecules of a gas may also be brought together by subjecting the gas to increased pressure at constant temperature, *i.e.*, by compression. If sufficient pressure can be exerted upon the gas, the molecules may be forced into such limited space that they may be caused to

assume the liquid condition. There is, however, a serious limitation on the use of this method. For every gas there is a temperature above which that gas cannot be liquefied by the application of pressure alone. This is known as the *critical temperature*. The critical temperatures of a few common gases are given in Table 8.

TABLE 8

CRITICAL TEMPERATURES OF GASES

Gas	Critical Temperature, °C.
Nitrogen	−147.1
Oxygen	−118.0
Carbon dioxide	31.35
Ammonia	132.4
Water	374.0

If the temperature of carbon dioxide gas, for example, is above 31.35°C., that gas cannot be liquefied by pressure alone no matter how great a

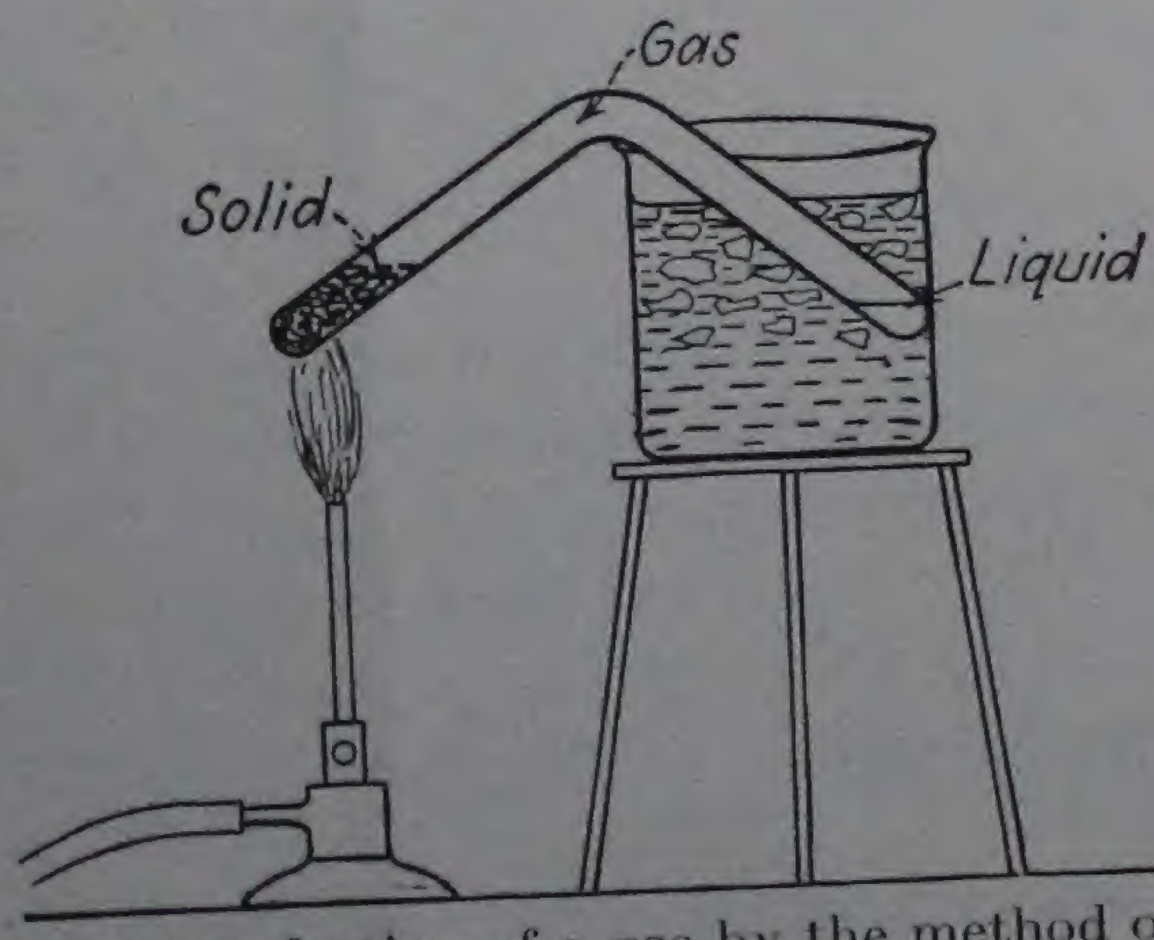

FIG. 40. Liquefaction of a gas by the method of Faraday.

pressure might be exerted upon it. Above 31.35°, the kinetic energy of the carbon dioxide molecules is so great that they cannot be brought sufficiently close together solely by compression. The pressure necessary to liquefy a gas *at* its critical temperature is known as the *critical pressure*.

The combined effects of decrease in temperature and increase in pressure are illustrated by the liquefaction of ammonia, as shown in Fig. 40. A substance that, when heated, liberates ammonia gas is placed in a bent glass tube, and both ends of the tube are closed. One end of the tube is cooled in ice water. Ammonia is liberated as a gas by heating the solid in the other end of the tube. As the gas is liberated, the pressure within the tube increases, and this, together with

the cooling provided at one end of the tube, causes droplets of the liquefied gas to appear in the cold region of the tube.

7.2. Industrial Applications

The liquefaction of gases is an important commercial problem. Most of the gases produced and sold commercially are liquefied and stored in the liquid condition in heavy-walled steel cylinders. The industrial liquefaction of air (and other gases) employs the combined effects of cooling and compression. Advantage is taken of the fact that, when a cooled compressed gas is allowed to expand either with or without the performance of work, the gas becomes cooler.

Linde (or Hampson) Process. This process involves the expansion of cooled compressed gases without the performance of work and

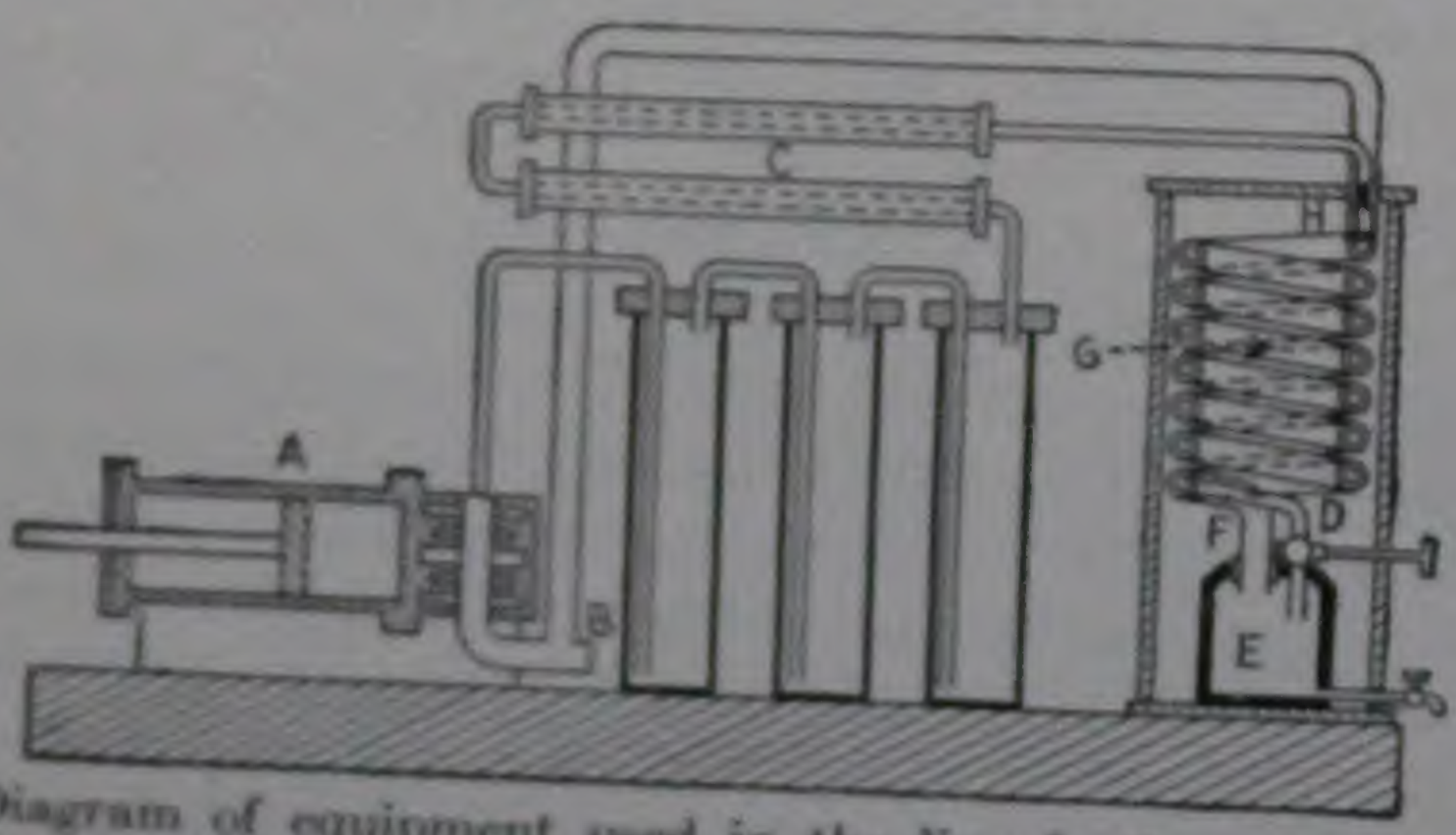

Fig. 41. Diagram of equipment used in the liquefaction of air by the Linde process.

is best described by reference to Fig. 41. After partial removal of carbon dioxide and water vapor, the air to be liquefied enters at *B* and is compressed to about 200 atm. (3000 lb. per sq. in.) by the compressor *A*. The warm compressed gas passes through the trap, driers, carbon dioxide removers, and the coolers *C*, and at *H* enters the inner tube of a dual concentric tube system *G*, which is efficiently insulated by means of sheep's wool, feathers, or balsa wood. By opening the valve *D* slightly the compressed gas is cooled considerably as it is allowed to expand into the chamber *E* to atmospheric pressure without doing any mechanical work. The cooled gas passes out of the chamber *E* at *F* into the outer tube of the dual system *G*, and this serves to lower the temperature of the incoming compressed gas in the inner tubes. When this cooled compressed incoming gas expands at *D*, the temperature falls still lower. If this cycle is operated for some time, the temperature continues to drop steadily within the entire cooling system until

the gas liquefies in the receiving chamber E. For the liquefaction of air the required temperature is about $-190°C$.

The Claude Process. The fundamental principle underlying this process is again the effect of cooling; the cooling in this case, however, is brought about by the utilization of the two effects, (1) the cooling effect due to expansion alone and (2) the cooling effect due to the performance of work. This process begins to differ from the Linde process at the point D in Fig. 41. Here, instead of allowing the gas to expand into a chamber at atmospheric pressure, the gas is caused to operate an air engine of the piston or turbine type. In so doing, the gas is cooled both by the expansion effect and by the work effect. The cooled gas is then sent through the outer coil F (as in the Linde process) and the entire cycle repeated until the temperature is lowered sufficiently to permit liquefaction of the gas. The efficiency of this process is much greater than that of the Linde process.

LIQUIDS

The transition from gas to liquid has been shown to result in a close packing of the molecules. Since the molecules in liquids are already practically touching one another, the space between them is so small that liquids cannot be made to occupy much smaller volumes by the application of pressure. That is, liquids cannot be compressed to any extent comparable to that possible in the case of gases. Despite their crowded condition, however, the molecules in a liquid are capable of motion although only through small distances and at relatively low velocities. So restricted is this motion that it may be described properly as a sort of vibration. If a colored liquid that is soluble in water is placed at the bottom of a tall glass cylinder filled with clear water, the molecules of the colored liquid will in time be seen to diffuse throughout the entire body of the liquid, thus proving that molecular motion is possible but relatively slow.

7.3. Surface Tension

Some insight into the properties of liquids may be had by considering the forces that influence molecules in different regions in the body of a liquid. A molecule in the interior of a liquid is surrounded on all sides by other molecules and is attracted equally in all directions, as shown in Fig. 42. Such a molecule, however, experiences no net restraint from these attractive forces and is restricted in its motion through the liquid because of the frequency with which it experiences collision. A

molecule in the surface of the liquid is subject to an inequality of forces since there is no comparable attractive force directly above it. The attraction of the molecules in the body of the liquid tends to pull the molecule B into the body of the liquid. This force acting in an inward direction causes a liquid to present the least possible exposed surface and is called the *surface tension*. It is because of the surface tension that individual drops of liquid tend to assume a spherical shape (for a given volume, the sphere presents the least possible surface), as is shown by Fig. 43. The surface tension is also responsible for the fact that liquids rise in capillary tubes, that oil rises in a lampwick, that objects can float on the surface of a liquid such as water, etc.

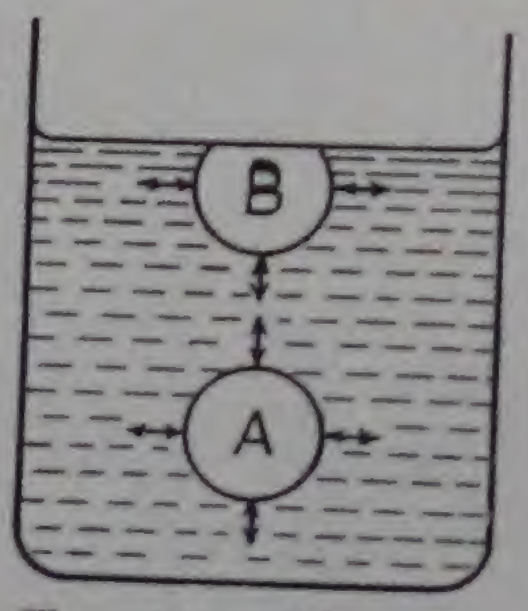

FIG. 42. Illustration of surface tension of a liquid.

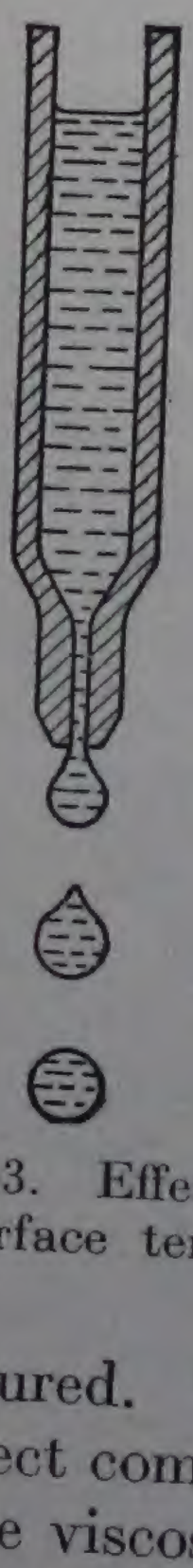
FIG. 43. Effect of surface tension.

7.4. Viscosity

A property which is possessed by both gases and liquids (both of which are *fluids*) but which is far more pronounced in liquids is that known as *viscosity*, which may be defined as "resistance to flow." Liquids that have a high viscosity and show relatively little tendency to flow when their containers are inverted are said to be *thick*, *heavy*, or *viscous* liquids, *e.g.*, molasses, tar, etc.

The viscosity of liquids may be compared conveniently by measuring the time required for given volumes of different liquids to flow from the same small orifice (Fig. 44). The glass container is supported in a vertical position and filled with a liquid. As the liquid flows from the container, the time required for the surface of the liquid to move from A to B is measured. Similar measurements with different liquids make possible a direct comparison.

The viscosity of a liquid depends upon the average velocity of the molecules, their size, and the distance between them. In the progress of liquid flow, these factors determine the ease with which molecules roll over one another. The greater size of the molecules present in lubricating oil is largely responsible for the fact that the lubricating oil is much more viscous than gasoline, which contains relatively smaller molecules. That the viscosity of liquids decreases with increase in temperature is shown by the fact that lubricating oil

becomes less viscous (thins out) at the operating temperature of a motor.

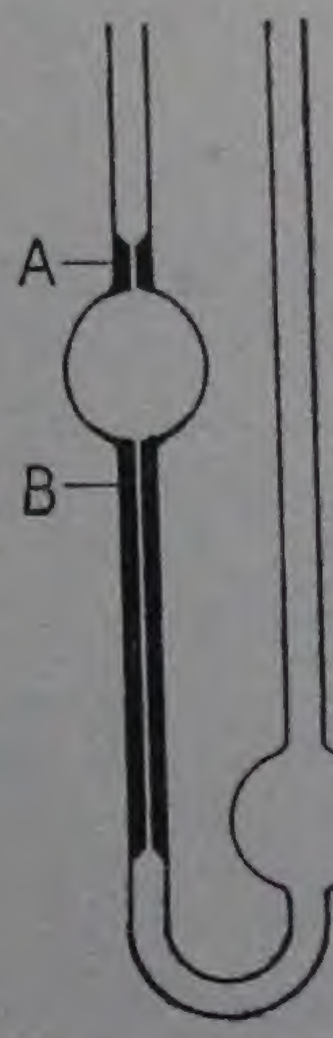

FIG. 44. A convenient type of apparatus for measurement of the viscosity of a liquid.

7.5. Vapor Pressure

Everyone is aware of the fact that, when water is allowed to stand exposed to the atmosphere, it *evaporates*. Further, it is known that water evaporates more rapidly the drier the atmosphere and the higher the temperature. Aside from the temperature effect, the rate at which water molecules leave the liquid and enter the vapor state depends upon the extent to which they are already present in the atmosphere.

If placed in a closed container at room temperature (Fig. 45), the water molecules still pass into the atmosphere above the liquid but cannot continue to do so indefinitely, *i.e.*, not all of the water can evaporate. As more and more molecules enter the vapor state against the opposing pressure of the air above the liquid, some of them in their motion through space strike the surface of and reenter the liquid. When the rate at which molecules return to the liquid is equal to the rate at which they leave the liquid, the two processes do not cease but continue to occur in opposite directions at the same rate.

$$H_2O_{liquid} \xrightarrow{\text{at rate } A} H_2O_{vapor}$$

$$H_2O_{vapor} \xrightarrow{\text{at rate } B} H_2O_{liquid}$$

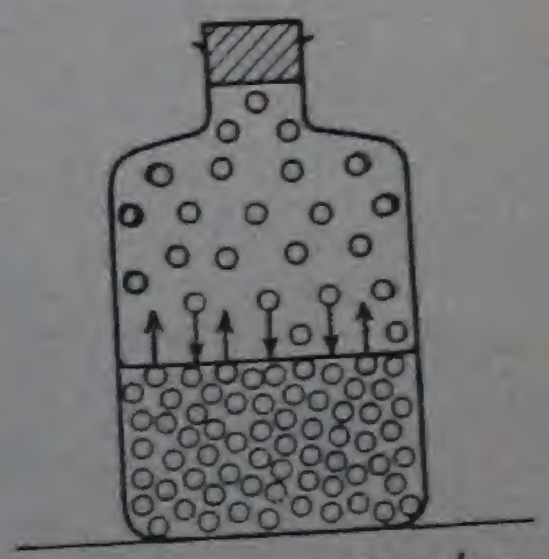

FIG. 45. Equilibrium between liquid water and water vapor.

At equilibrium:

$$\text{Rate } A = \text{rate } B$$

Thus is achieved a dynamic balance of opposing forces which is described as *dynamic equilibrium*. Under these conditions the space above the liquid is said to be *saturated* with water vapor. **The vapor pressure of a liquid is defined as the pressure exerted by the vapor upon the surface of the liquid when the two are in a condition of equilibrium.**

Some molecules in the body of a liquid are capable of escaping through the surface and into the vapor state because they have kinetic energies slightly greater than the average kinetic energy of all the

molecules. With increase in temperature, the kinetic energy of all the molecules is increased. All liquids tend to evaporate, but at markedly different rates; at the same temperature, gasoline evaporates much more rapidly than water. A liquid that evaporates readily must have a high vapor pressure and is said to be *volatile*.

7.6. Boiling Temperature

When a liquid such as water is heated in an open container, the heat energy that is supplied to the water increases the kinetic energy of the water molecules and in this way serves to increase the rate of evaporation. Since the water molecules leaving the surface of the liquid have increased kinetic energies, they are capable of doing work in pushing against the opposing atmospheric pressure. If the temperature of the water is increased sufficiently (to 100°C. at standard atmospheric pressure), the vapor pressure of the water becomes slightly greater than the opposing atmospheric pressure and the liquid is said to *boil*. The condition known as *boiling* is usually accompanied by the rise of bubbles of vapor from the body of the liquid. **The boiling temperature may be defined as the temperature at which the vapor pressure of a liquid just exceeds the opposing pressure of the atmosphere.** During the process of boiling, the heat supplied from the outside does not raise the temperature of the liquid but merely serves to accomplish the change in state from liquid to gas. The boiling temperature of a liquid is, of course, influenced by the magnitude of the opposing atmospheric pressure. At sea level, water boils at 100°C. while at the top of Mt. Everest (elevation about 29,000 ft. above sea level) water boils at 71°C. because the opposing pressure of the atmosphere is less at the higher altitude.

Although most liquids may be caused to boil at characteristically definite temperatures under normal conditions of pressure, some liquids decompose under the influence of heat before their boiling temperatures can be reached. Even certain of these, however, can be caused to boil without decomposition if the opposing pressure is lowered to a sufficient extent, thus enabling the liquids to boil at temperatures below their decomposition temperatures.

7.7. Freezing Temperature

Reference has been made in the preceding pages to the fact that liquid water changes to solid ice at 0°C. and that liquid oxygen solidifies at a temperature of −218.4°C. For most liquids there are characteristic and definite temperatures at which these liquids freeze or

solidify. In most cases, when a liquid is cooled to its freezing temperature, solid *crystals* appear and at that temperature exist in equilibrium with the liquid. **The freezing temperature may be defined as that temperature at which the liquid and solid forms of a pure substance can exist together without change in temperature.** All liquids that solidify to form crystalline solids have definite freezing temperatures.

Manufacture of Ice. The principles employed in the commercial manufacture of ice are concerned with the fact that a gas is cooled by expansion and that the evaporation of a liquid withdraws heat from its

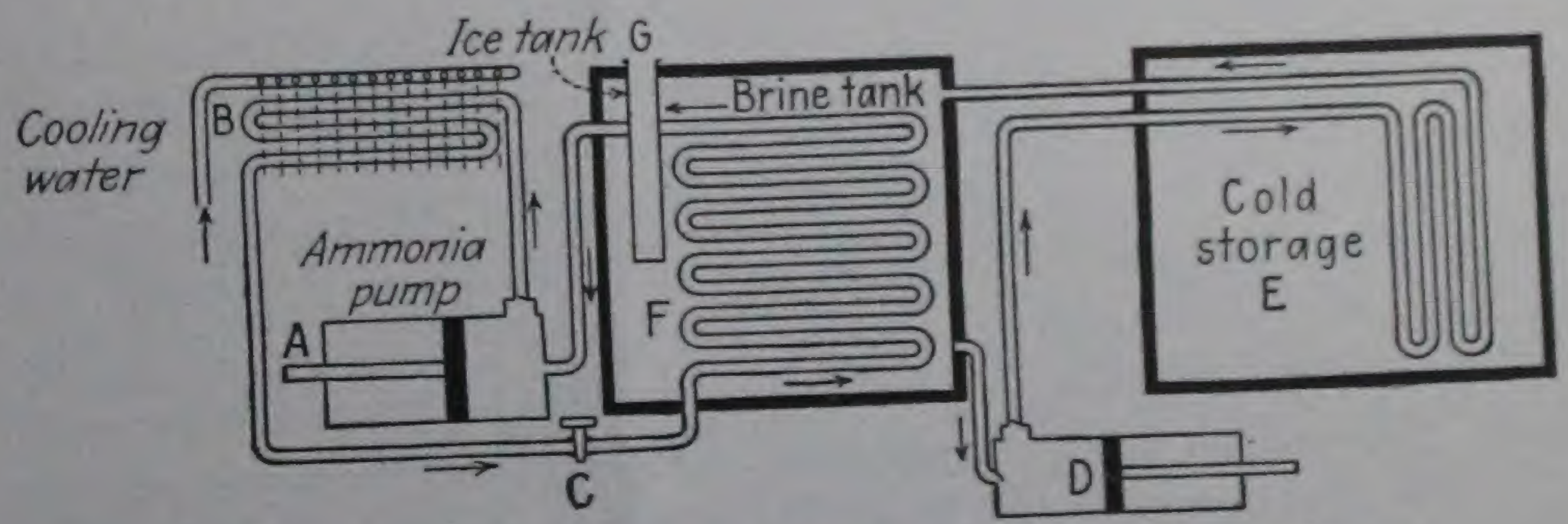

FIG. 46. Combined ice-making and cold-storage system.

surroundings. A combined ice-making and cold-storage system is illustrated in Fig. 46. Ammonia gas is compressed by the pump *A* and is forced into the coils cooled by water sprayed from the pipe *B*. Under the combined effects of pressure and cooling, the ammonia liquefies and is forced through the valve *C* and into coils *F* immersed in brine. Here, the liquefied gas vaporizes and in so doing withdraws heat from the brine, thus lowering the temperature sufficiently to freeze the water contained in the ice tank *G*, which is also immersed in the brine. The gaseous ammonia is then returned to the compressor *A* and goes through the same cycle again and again. By pumping the cold brine (by means of the pump *D*) through the coils in the storage unit *E* at any desired rate, a low temperature may be maintained in the cold-storage compartment. Except for minor operative details, the same type of apparatus is employed in the small refrigeration units used in the home. Gases other than ammonia may be employed. For example, dichlorodifluoromethane, or *Freon* (CCl_2F_2), and other similar compounds are the gases most widely used in household refrigeration units.

SOLIDS

The conversion of a gas to a liquid has been seen to result in a profound restriction upon the motion of the molecules concerned. This restriction becomes still more pronounced when a liquid solidifies. The fixed physical form of solids and many other properties that characterize matter in the solid state are by-products of restricted molecular motion.

7.8. Melting Temperature[1]

When heat is supplied to a crystalline solid which is not decomposed by heat, the temperature of the solid is increased until sufficient to cause the solid to *melt*. Further application of heat serves only to change the solid into the liquid condition. Obviously, the melting temperature of a pure solid such as ice is the same as the freezing or solidification temperature of the corresponding pure liquid (water) and is amenable to the same definition. The process of melting requires that the kinetic energy of the molecules of the solid be increased (by supplying energy in the form of heat) to such point that the molecules may be capable of motion to the extent normally possible in the liquid state.

7.9. Vapor Pressure

Some solids neither decompose nor melt when heated. Even at ordinary temperatures such solids have a pronounced tendency to evaporate. When the vapors come into contact with a cooled surface, they return directly to the solid condition. In Chap. 1 this change in state from solid to gas to solid was defined as *sublimation*, and solids that behave in this manner are said to *sublime*. Iodine, camphor, and "moth balls" [naphthalene ($C_{10}H_8$) and paradichlorobenzene($C_6H_4Cl_2$)] are common examples of solids that sublime readily. In all but a relatively small number of cases, the vapor pressure of solids is so small as to be negligible.

7.10. Crystalline Solids

The formation of a crystal upon solidification of a liquid requires that the molecules be arranged in *patterns of definite geometric form*

[1] Temperatures of boiling, freezing, or melting are commonly referred to in a rather loose fashion as *points*. Thus, chemists speak of *boiling points*, *melting points*, etc.

under the influence of forces of attraction or cohesion. With respect to each other, the molecules occupy essentially fixed positions in space, and molecular motion is possible only in an extremely small measure. Depending upon the type of crystal concerned, the units of matter that make up the crystal may be molecules, atoms, or ions.

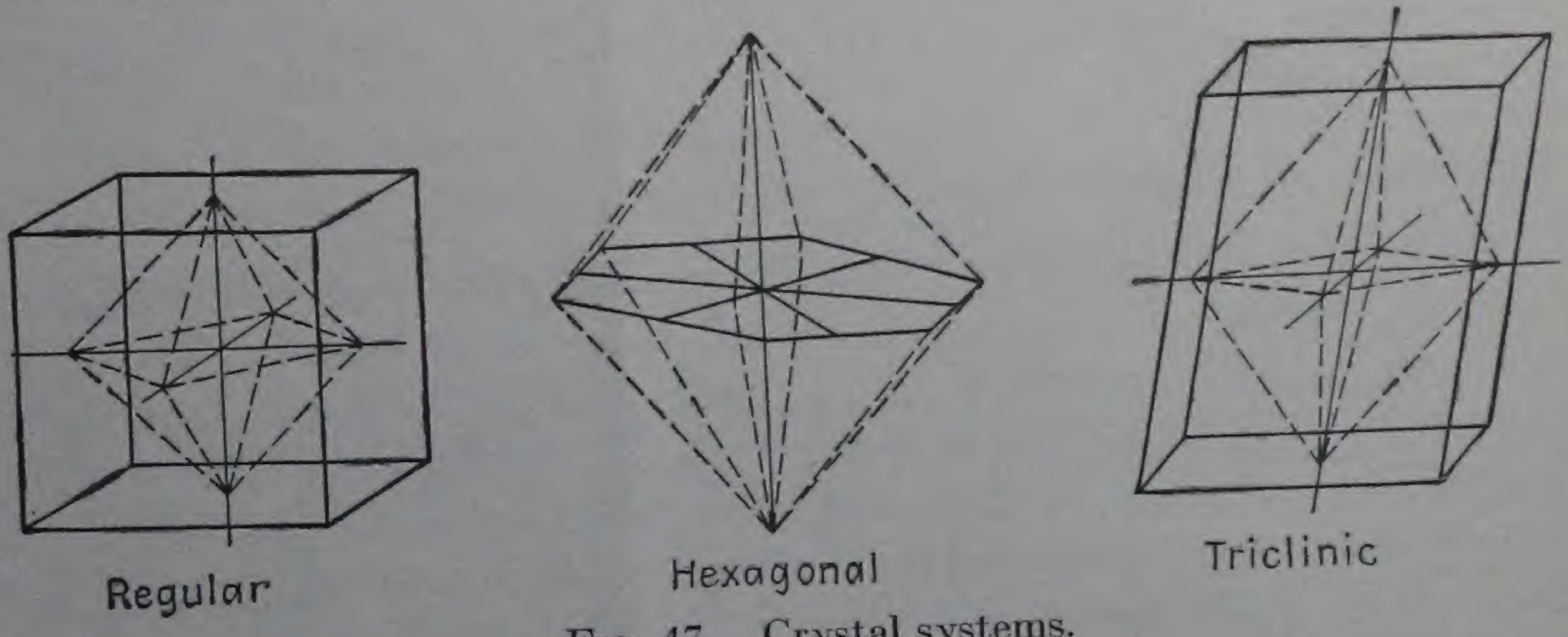

FIG. 47. Crystal systems.

The particular pattern in which the molecules, atoms, or ions are arranged within the crystal determines the *external form* of the whole crystal. The known forms or systems in which crystalline solids exist are six in number, three of which are illustrated in Fig. 47. Crystalline solids exhibit definite planes of cleavage and have definite melting temperatures.

Structure of Crystals. Present-day knowledge of the *internal structure* of crystals is the result of joint efforts of chemists and physicists. The experimental tool most useful in investigating the architecture of matter in the crystalline condition has been and is the X ray. By studying the manner in which X rays are reflected by crystals, much has been learned concerning the arrangement of the atoms, molecules, or ions with respect to one another. In the regular or cubic sys-

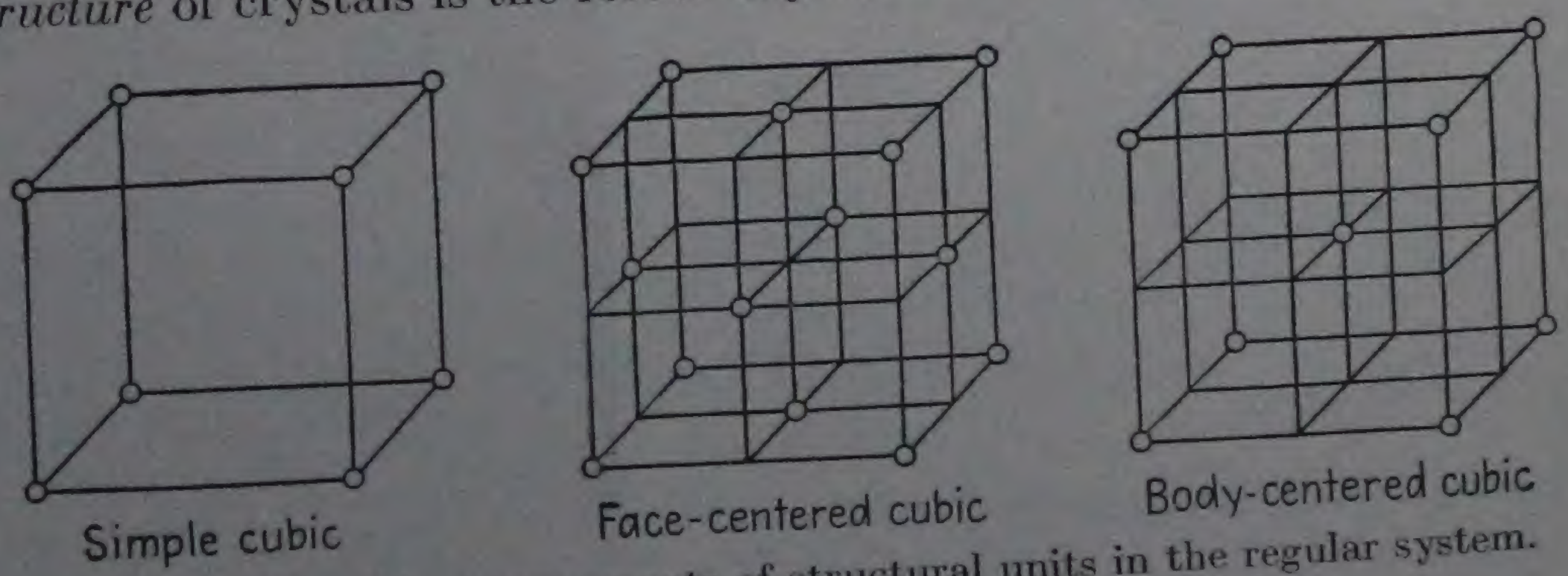

FIG. 48. Possible arrangements of structural units in the regular system.

tem (Fig. 47) the structural units may be arranged in the three patterns shown in Fig. 48. The structures of a number of common crystalline substances are shown in Fig. 49.

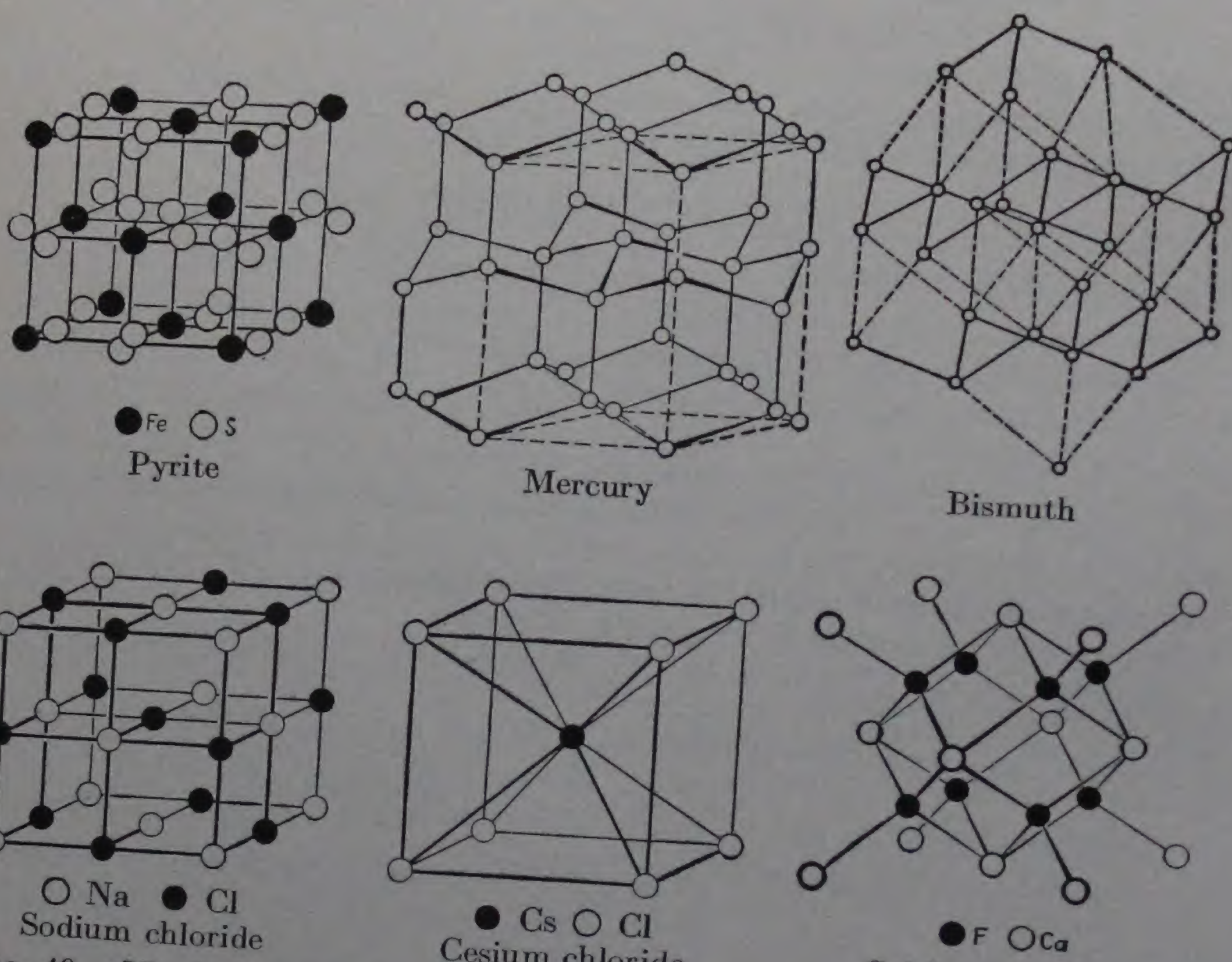

FIG. 49. The lattice structures of common crystals. (*Courtesy of Seilz, Modern Theory of Solids, McGraw-Hill Book Company, Inc.*)

7.11. Amorphous Solids

Upon being cooled, some liquids fail to crystallize. They become more and more viscous until finally they exist in a solid condition. Pitch, tar, and glass are examples of such materials. These solids are described by the term *amorphous*, which is derived from the Greek word meaning "without form." Amorphous solids are characterized by the absence of any definite geometric arrangement of structural units and by the fact that they soften gradually upon being heated. They do not melt sharply at definite temperatures as do crystalline solids.

GENERAL EXERCISES

1. Define the following terms: (*a*) critical temperature, (*b*) critical pressure, (*c*) surface tension, (*d*) viscosity, (*e*) vapor pressure, (*f*) dynamic equilibrium, (*g*) boiling temperature, (*h*) freezing temperature, (*i*) melting temperature.

2. What is meant by the expressions: (*a*) a volatile liquid, (*b*) a viscous liquid, (*c*) an amorphous solid, (*d*) a crystalline solid?

3. Why will a liquid boil at a lower temperature in a partial vacuum than at atmospheric pressure?

4. If a current of air is passed over the surface of a liquid, the rate of evaporation is increased. Explain.

5. What relationship exists between the vapor pressure of liquids and their boiling temperatures?

SUGGESTED READING

Journal of Chemical Education

Cady, Liquid Air, **8,** 1027 (1931).

Reinmuth, Cooling and Refrigeration, **6,** 1768 (1929).

Denues, Liquid Oxygen Explosives, **18,** 45 (1941).

Evans, Refrigeration, **19,** 539 (1942).

Brescia, The Critical Temperature, **24,** 123 (1947).

Hauser, A Simple Method of Building Close-packed Molecular and Crystal Models, **18,** 164 (1941).

Seymour, A Simple Method of Crystal Model Construction, **15,** 192 (1938).

Huggins, The Structure of Crystals, **4,** 73 (1927).

Stilwell, Crystal Chemistry, **10,** 590, 667 (1933); **11,** 159 (1934); **13,** 415, 469, 521, 566 (1936); **14,** 34, 131 (1937).

Brown, The Atomic Arrangement in the Sulfur Unit Cell, **18,** 182 (1941).

CHAPTER 8
RELATIVE WEIGHTS OF MOLECULES

In Chap. 1 it was pointed out that the molecules of elemental gases, such as hydrogen, nitrogen, and chlorine, consist of 2 atoms each, H_2, N_2, Cl_2, etc. Since some information concerning the nature and behavior of gases in terms of the kinetic-molecular theory has been acquired, it now becomes possible to supply proof of the correctness of these formulas. The problem of deciding upon the number of atoms present in a given molecule is, of course, essentially the same as that involved in determining the relative weight of the particular molecule. If a hydrogen molecule contains 2 atoms, then the relative weight of the hydrogen molecule is 2.016 (*i.e.*, 2×1.008) based on the standard $O = 16$. But suppose that the number of atoms in the hydrogen molecule was unknown. This situation would require that the relative weight of the hydrogen molecule be determined by experiment in the laboratory. Methods are available whereby the molecular weights of both elemental and compound gases (as well as liquids and solids) may be measured by experiment.

8.1. Avogadro's Law

In 1811, the Italian physicist Avogadro voiced a prediction to the effect that **at the same temperature and pressure, equal volumes of all gases contain the same number of molecules.** At the time, Avogadro's prediction was perhaps nothing more than a reasonable supposition or guess. In subsequent years, however, the truth of this statement has been so firmly established that it has come to be known as Avogadro's *law*.

The far-reaching importance of Avogadro's law lies in the fact that it provides a concrete relationship between molecules (which are invisible) and the volumes that they occupy. While the scientist cannot work with individual molecules, he can manipulate definite volumes of gases which have real meaning in terms of the numbers of molecules present. A knowledge of the density of gases (Sec. 6.11) together with Avogadro's law makes possible a direct comparison of the weights of gaseous molecules.

Consider the volume occupied by a gas at standard conditions to be 1 liter, and represent the number of molecules by n. Since the density of hydrogen, for example, is known to be 0.0899 g. per liter at S.T.P., then the absolute weight in grams of the individual hydrogen molecule must be

$$\text{Wt. of 1 hydrogen molecule} = 0.0899 \div n$$

Similarly, from the known density of oxygen,

$$\text{Wt. of 1 oxygen molecule} = 1.4290 \div n$$

From this information, it is seen that the ratio of the weights of the individual molecules is

$$\frac{\text{Wt. of 1 oxygen molecule}}{\text{Wt. of 1 hydrogen molecule}} = \frac{1.4290 \div n}{0.0899 \div n} = \frac{1.4290}{0.0899} = \frac{15.88}{1}$$

This result is simply a *comparison* of the absolute weights of the molecules of oxygen and hydrogen and provides the information that the oxygen molecule is 15.88 times as heavy as the hydrogen molecule.

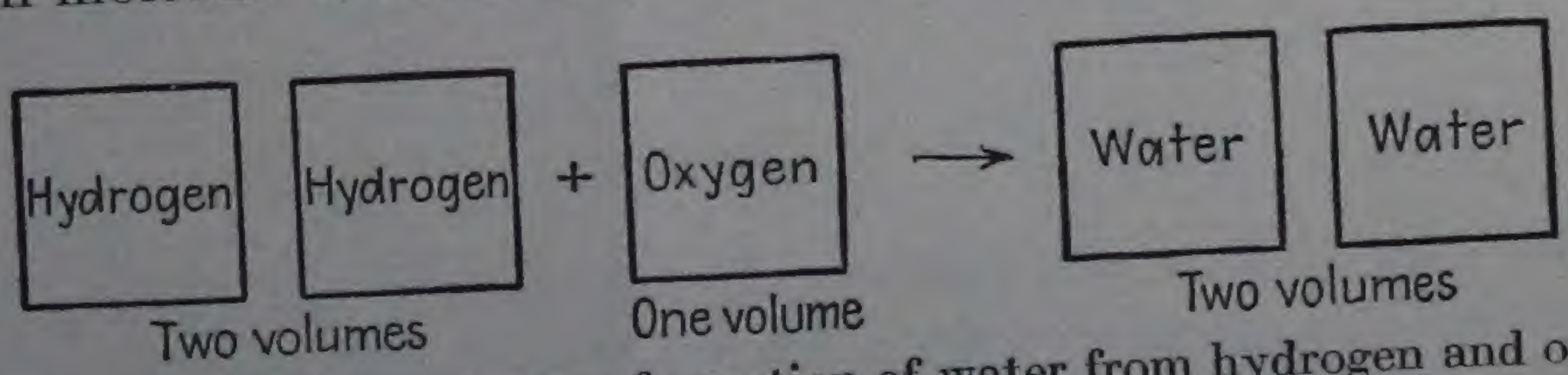

FIG. 50. Combining volumes: formation of water from hydrogen and oxygen.

Since the relative weights of atoms are based on the arbitrarily selected standard of O = 16, the relative weights of molecules should be expressed on the same basis. If the relative weight of either the hydrogen or oxygen molecule were known, then the foregoing ratio could be used to calculate the molecular weight of the other.

8.2. Gay-Lussac's Law

Three years before the first enunciation of Avogadro's law, Gay-Lussac observed that there is a simple relationship between the volumes of gases that combine in or are produced by chemical reactions. For example, at the same temperature and pressure, two volumes of hydrogen combine with one volume of oxygen to form two volumes of water

vapor (Fig. 50). Similarly, when solid sulfur is burned in oxygen, one volume of oxygen produces one volume of sulfur dioxide (Fig. 51). One volume of hydrogen and one volume of chlorine unite to form two volumes of hydrogen chloride (Fig. 52), and three volumes of hydrogen and one volume of nitrogen combine to form two volumes of ammonia (Fig. 53). From many such observations, Gay-Lussac formulated a law to the effect that **at the same temperature and pressure, the**

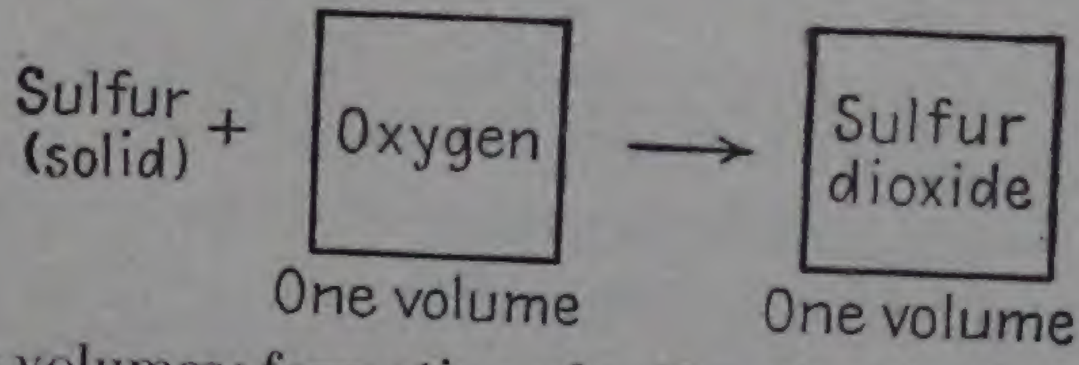

FIG. 51. Combining volumes: formation of sulfur dioxide from sulfur and oxygen.

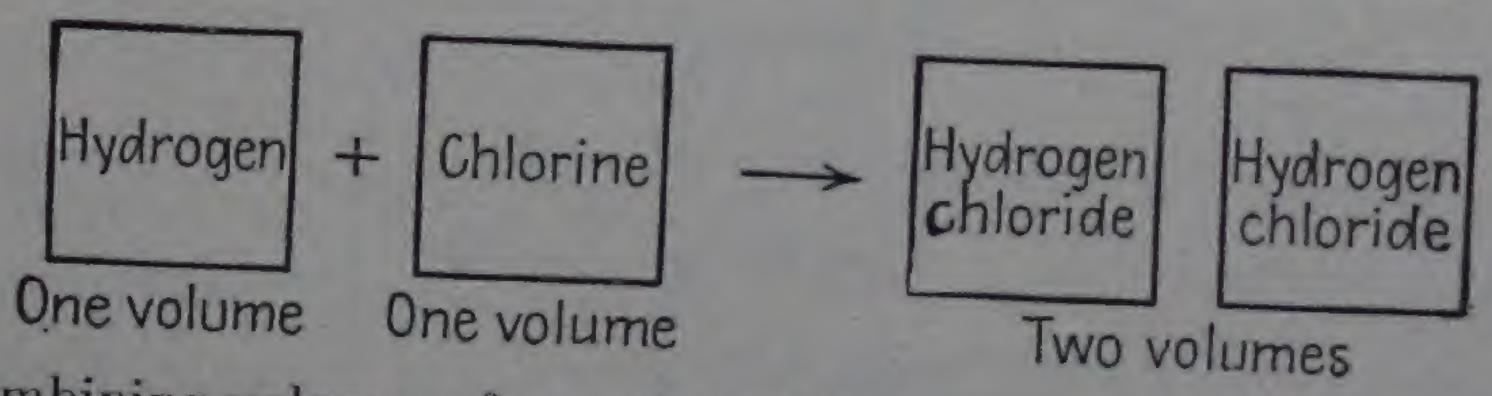

FIG. 52. Combining volumes: formation of hydrogen chloride from hydrogen and chlorine.

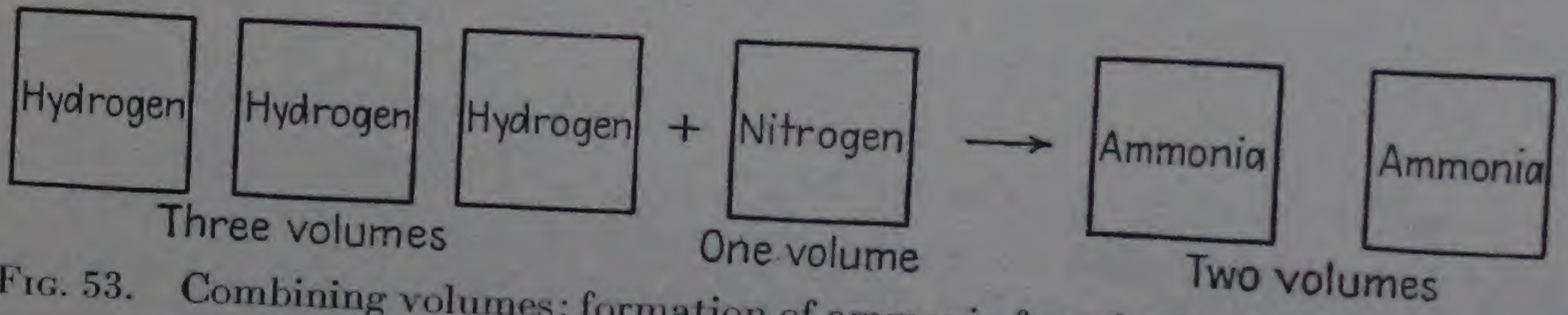

FIG. 53. Combining volumes: formation of ammonia from hydrogen and nitrogen.

ratio by volume in which gases combine in or are produced by chemical reactions may be expressed by small whole numbers. Thus, the ratios of the volumes of gases concerned in the reactions illustrated by Figs. 50 to 53, may be expressed as

$$\text{Hydrogen : oxygen : water vapor} = 2:1:2$$
$$\text{Oxygen : sulfur dioxide} = 1:1$$
$$\text{Hydrogen : chlorine : hydrogen chloride} = 1:1:2$$
$$\text{Hydrogen : nitrogen : ammonia} = 3:1:2$$

Together, the laws of Avogadro and Gay-Lussac make possible the proof of the statement that the molecules of some elemental gases contain at least 2 atoms each.

8.3. Composition of Simple Gas Molecules

By reference to Fig. 52, it is seen that one volume of hydrogen and one volume of chlorine combine to form two volumes of hydrogen chloride. At the same temperature and pressure, each of these volumes must (according to Avogadro's law) contain the same number of molecules. If it is assumed that these volumes are of such size that each contains exactly 1000 molecules, then the reaction may be represented as shown in Fig. 54. Attention must now be focused on the 2000 molecules of hydrogen chloride. Since hydrogen chloride is a compound containing hydrogen, each individual molecule of it must contain some hydrogen. The smallest "piece" of hydrogen that can

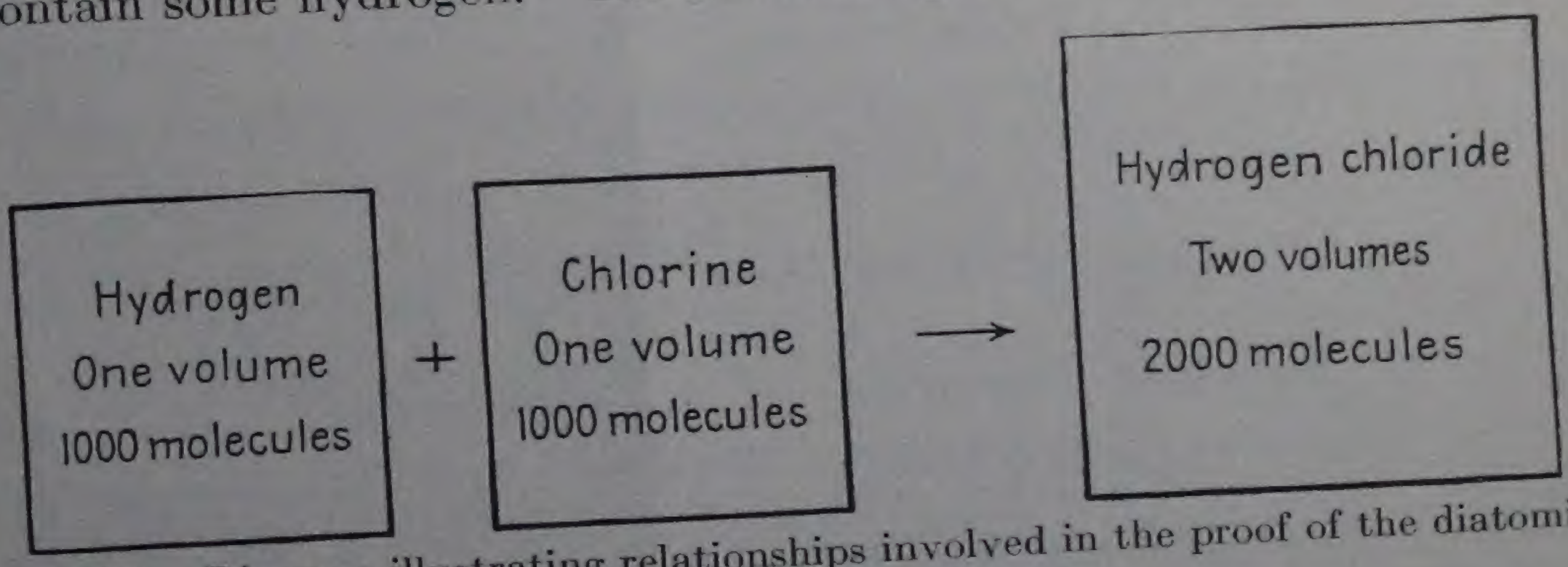

FIG. 54. Diagram illustrating relationships involved in the proof of the diatomic nature of simple gas molecules.

be present in a molecule of any compound must be an *atom* of hydrogen (see definition of the term *atom*, Sec. 1.12). Therefore, the 2000 molecules of hydrogen chloride must contain *at least* 2000 atoms of hydrogen. *The* 2000 *atoms of hydrogen had to come from only* 1000 *molecules of hydrogen.* The inescapable conclusion is that each of the 1000 molecules of hydrogen must have contained at least 2 atoms.

The same line of reasoning may be applied in the case of chlorine, or in the case of reactions involving other simple gases. This procedure does not in itself prove that the number of atoms in these molecules may not be greater than two, but it does prove that the number must be *at least* two. By a variety of experimental methods, which need not be discussed here, the correctness of the number two has been firmly established.

8.4. Molecular Weight of Oxygen

In the preceding section it was concluded that the hydrogen molecule contains 2 atoms. On the scale of relative atomic weights already established, the relative weight of the hydrogen atom is 1.008. Consequently, the relative weight of the hydrogen molecule must be 2×1.008 or 2.016.

In Sec. 8.1, Avogadro's law was used to show that the oxygen molecule is 15.88 times as heavy as the hydrogen molecule. Hence, the relative weight of the oxygen molecule must be 15.88×2.016, or 32. The correctness of this result may be confirmed by (1) direct measurement of the molecular weight of oxygen by suitable laboratory experiments and (2) proving (by the method outlined in Sec. 8.3) that the oxygen molecule contains at least 2 atoms and recalling that the relative atomic weight of oxygen is 16.

8.5. Determination of Molecular Weights by Experiment

Calculation of the ratios of the molecular weights of gases has shown that, at the same temperature and pressure, the molecular weights of different gases bear to each other the same relationship as that between the weights of equal volumes of the gases. If, then, the weight of a known volume of a gas is determined (by direct weighing) in the laboratory, the molecular weight of the gas may be calculated in relation to the weight of the same volume of a gas of known molecular weight.

Suppose, for example, that 55.3 cc. of pure dry nitrogen is weighed by means of an accurate balance and found to weigh 0.0625 g. in a laboratory in which the temperature is 26°C. and the barometric pressure is 752 mm. Under standard conditions, this weight of nitrogen occupies a volume given by

$$\begin{aligned} V_{\text{S.T.P.}} &= 55.3 \times {}^{273}\!/_{299} \times {}^{752}\!/_{760} \\ &= 50 \text{ cc.} \end{aligned}$$

If 50 cc. of nitrogen at S.T.P. weighs 0.0625 g., then 1 liter of the gas must weigh 1.2505 g. under the same conditions.

$$0.0625 \times {}^{1000}\!/_{50} = 1.2505 \text{ g.}$$

One liter of hydrogen (molecular weight = 2.016) at S.T.P. weighs 0.0899 g. Therefore,

$$\frac{\text{Mol. wt. of nitrogen}}{\text{Mol. wt. of hydrogen}} = \frac{\text{wt. of 1 liter of nitrogen}}{\text{wt. of 1 liter of hydrogen}}$$

Substituting,

$$\frac{\text{Mol. wt. of nitrogen}}{2.016} = \frac{1.2505}{0.0899}$$

$$\begin{aligned} \text{Mol. wt. of nitrogen} &= 2.016 \times \frac{1.2505}{0.0899} \\ &= 28 \end{aligned}$$

This experimental result is confirmed when it is recalled that the molecule of nitrogen contains 2 atoms, each having a weight of 14 units in relation to O = 16.

Molecular Weights of Compound Gases. The discussion and examples previously given have been restricted to elemental gases. That the molecular weights of compound gases may be calculated from experimental data in the same manner is shown by the following example. By a similar experiment, a known volume of sulfur dioxide gas was found to weigh 0.07428 g. Corrected to standard conditions, this sample occupied a volume of 26 cc., from which it was calculated that 1 liter of sulfur dioxide gas at S.T.P. weighs 2.8572 g. The molecular weight of sulfur dioxide is given by

$$\frac{\text{Mol. wt. of sulfur dioxide}}{2.016} = \frac{2.8572}{0.0899}$$

$$\text{Mol. wt. of sulfur dioxide} = 2.016 \times \frac{2.8572}{0.0899}$$

$$= 64$$

At this point it might appear to the student that all of this is unnecessary. After all, sulfur dioxide has the formula SO_2; the atomic weight of sulfur is 32, that of oxygen is 16, and it follows that the molecular weight of sulfur dioxide is $32 + (2 \times 16) = 64$. But suppose that, as is often the case, the true formula is not known. Compounds hitherto unknown in the experience of man are discovered in the laboratory every day. The following outline of a typical situation serves to establish the need for methods that permit the calculation of molecular weights from experimental data.

A new chemical compound was produced in the laboratory and found by qualitative analysis to contain only the elements carbon and hydrogen. Quantitative analysis showed that this compound consisted of 82.76 per cent of carbon and 17.24 per cent of hydrogen. From this information, the simplest formula (Sec. 3.4) was shown to be C_2H_5, *i.e.*, carbon atoms and hydrogen atoms were shown to be present in the ratio of 2 to 5. But this same ratio is maintained in all the compounds having the formulas (and molecular weights) listed below.

Compound	Mol. wt.	C/H ratio
C_2H_5	29	$\frac{2}{5}$
C_4H_{10}	58	$\frac{2}{5}$
C_6H_{15}	87	$\frac{2}{5}$
C_8H_{20}	116	$\frac{2}{5}$

Obviously, a knowledge of the molecular weight of the new compound is required before a decision as to the correct formula can be made. By the method previously described, this particular compound was found to have a molecular weight of 58, from which it followed that the correct formula was C_4H_{10}.

8.6. Gram-molecular Volume

Knowing the densities and molecular weights of a number of simple and compound gases, it becomes of interest to calculate the volume which, at standard conditions, contains *exactly one gram-molecular weight of each gas.* The data necessary for such calculations are assembled in Table 9.

TABLE 9
DENSITIES AND GRAM-MOLECULAR WEIGHTS OF SOME COMMON GASES

Gas	Mol. wt.	Density, g. per liter at S.T.P.
Hydrogen (H_2)	2.016	0.0899
Methane (CH_4)	16.031	0.7168
Ammonia (NH_3)	17.031	0.7710
Nitrogen (N_2)	28.016	1.2505
Hydrogen sulfide (H_2S)	34.016	1.5390
Chlorine (Cl_2)	70.914	3.2140

If 0.0899 g. of hydrogen occupies a volume of 1000 cc. at S.T.P., then the volume that is occupied by 2.016 g. of hydrogen under the same conditions of temperature and pressure is

$$\frac{V}{2.016} = \frac{1000}{0.0899}$$

$$V = \frac{1000 \times 2.016}{0.0899}$$

$$= 22{,}400 \text{ cc., or } 22.4 \text{ liters}$$

Thus, if one should fill a container of 22.4 liters volume with hydrogen at 0° and 760 mm., there would be contained therein exactly 1 gram-molecular weight of hydrogen.

Similar calculations, in abbreviated form, are given below for each of the other five gases listed in Table 9.

For methane:

$$V = \frac{1000 \times 16.031}{0.7168}$$

$$= 22{,}400 \text{ cc., or } 22.4 \text{ liters}$$

For ammonia:

$$V = \frac{1000 \times 17.031}{0.7710}$$

$$= 22{,}400 \text{ cc., or } 22.4 \text{ liters}$$

For nitrogen:

$$V = \frac{1000 \times 28.016}{1.2505}$$

$$= 22{,}400 \text{ cc., or } 22.4 \text{ liters}$$

For hydrogen sulfide:

$$V = \frac{1000 \times 34.016}{1.5390}$$

$$= 22{,}400 \text{ cc., or } 22.4 \text{ liters}$$

For chlorine:

$$V = \frac{1000 \times 70.914}{3.2140}$$

$$= 22{,}400 \text{ cc., or } 22.4 \text{ liters}$$

This striking result is not accidental. The gases for which these calculations are made were chosen at random, and this list of gases and

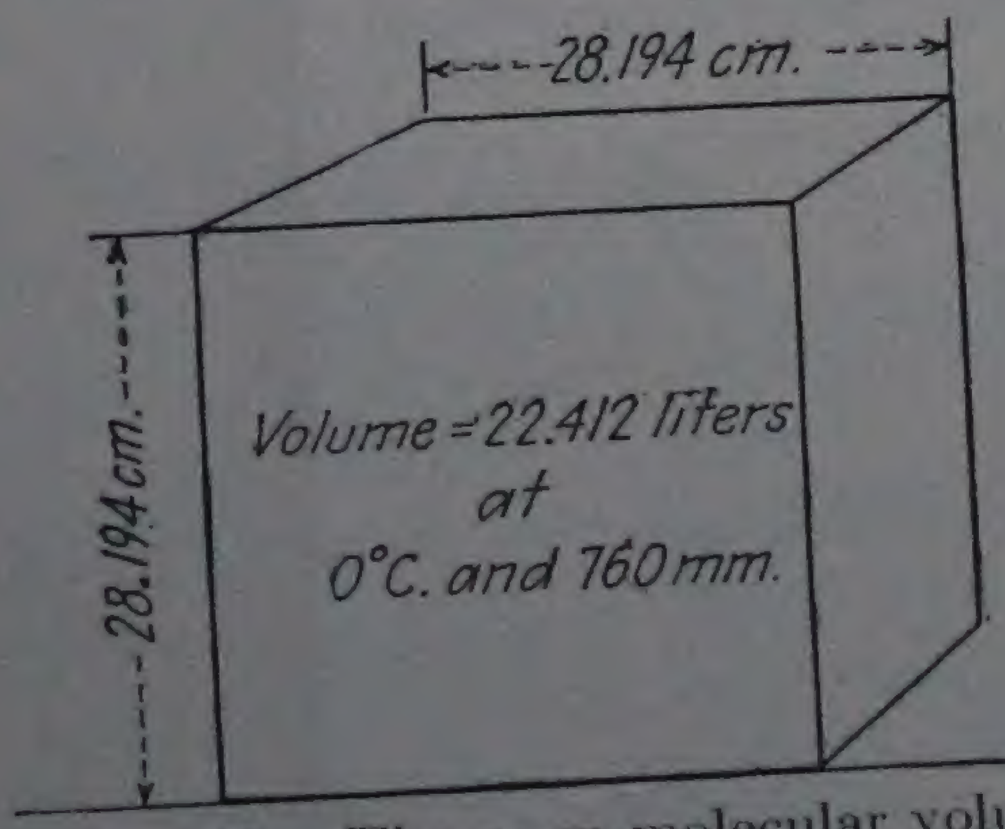

FIG. 55. The gram-molecular volume.

the corresponding calculations could be extended indefinitely, always with the same result.

This volume of 22.4 liters is known as the **gram-molecular volume** and is commonly abbreviated as G.M.V. It is that volume which under standard conditions contains exactly 1 gram-molecular weight

of any gas, either elemental or compound. The volume of 22.4 liters is approximately ¾ cu. ft. and is represented exactly (Fig. 55) by a cube with 28.194 cm. edge (inside measurement).

8.7. Use of the Gram-molecular Volume in the Solving of Practical Problems

The gram-molecular volume is a perfectly definite relationship between weight and volume. Through its use, the chemist solves with ease many problems which are frequently encountered in practical applications of chemistry and which might otherwise be more difficult or at least more time-consuming.

Calculation of Molecular Weights. In Sec. 8.5, there was outlined for the calculation of molecular weights a method that depended upon a comparison with the weight of an equal volume of another gas of known molecular weight. By this method, the molecular weights of nitrogen and sulfur dioxide were calculated by using hydrogen as a reference substance. Although this method is perfectly sound, it does require that one remember (or look up in handbooks where such data are tabulated) the weight of 1 liter or the weight of some other definite volume of hydrogen.

In Sec. 8.5, it was shown that a given sample of nitrogen weighs 0.0625 g. and occupies a volume of 50 cc. at S.T.P. This fact together with the gram-molecular volume is all the information required to calculate the weight of nitrogen contained in 22.4 liters, which weight is, of course, the gram-molecular weight of nitrogen.

$$\frac{\text{Mol. wt. of nitrogen}}{22{,}400 \text{ cc.}} = \frac{0.0625}{50}$$

$$\text{Mol. wt. of nitrogen} = \frac{0.0625 \times 22{,}400}{50}$$

$$= 28$$

In a similar manner, the molecular weight of the compound gas sulfur dioxide is calculated. If at S.T.P. 0.07428 g. of sulfur dioxide occupies a volume of 26 cc., then the molecular weight of this gas is given by

$$\text{Mol. wt. of sulfur dioxide} = \frac{0.07428 \times 22{,}400}{26}$$

$$= 64$$

Calculation of Weight of a Gas Contained in Any Specified Volume under Any Experimental Conditions. For use in a given

experiment, a chemist needed 2000 g. of hydrogen sulfide gas. The only hydrogen sulfide that was available was that contained in a 150-liter tank at a pressure of 10 atm. and at 30°C. The question was whether the *weight* of hydrogen sulfide in the tank was sufficient for the experiment.

The answer to this question may be had by the use of the gram-molecular-volume relationship. At S.T.P., the hydrogen sulfide contained in this tank would occupy a volume of

$$V_{\text{S.T.P.}} = 150 \times \frac{273}{303} \times \frac{10 \times 760}{760}$$

$$= 1350 \text{ liters}$$

But 22.4 liters of hydrogen sulfide (at S.T.P.) weighs 34.016 g. (the gram-molecular weight of hydrogen sulfide). The weight of H_2S in the tank is therefore readily calculated as follows:

$$\frac{\text{Wt. of } H_2S}{1350} = \frac{34.016}{22.4}$$

$$\text{Wt. of } H_2S = 1350 \times \frac{34.016}{22.4}$$

$$= 2050 \text{ g.}$$

or 50 g. in excess of the required amount.

To consider another example, assume that, in order to calculate the relative density of the gas known as phosphine (PH_3), it is convenient to know the weight of 1 liter of this gas at S.T.P. The molecular weight of phosphine is 34.024, which is the weight contained in 22.4 liters of PH_3 at S.T.P. Hence,

$$\text{Wt. of 1 liter of } PH_3 = \frac{34.024}{22.4}$$

$$= 1.5189 \text{ g.}$$

Calculation of Volumes of Gases Consumed in or Produced by Chemical Reactions. The union of iron and oxygen may be represented by the following equation:

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3$$

If one wished to know the *volume* of oxygen required to burn a given quantity of iron, the *weight* of oxygen could be calculated and divided by the weight of 1 liter of oxygen to find the volume required.

However, a simpler procedure is now available. The equation provides the information that the burning of 4 gram atoms of iron ($4 \times 55.84 = 223.36$ g.) requires 3 gram-molecular volumes of oxygen ($3 \times 22.4 = 67.2$ liters) at S.T.P. Hence, the volume of oxygen required to burn, for example, 266 g. of iron may be calculated as follows:

$$\frac{\text{Vol. of } O_2}{266} = \frac{67.2}{223.36}$$

$$\text{Vol. of } O_2 = 266 \times \frac{67.2}{223.36}$$

$$= 80 \text{ liters}$$

With the volume at S.T.P. known to be 80 liters, the volume under any other conditions of temperature and pressure may be calculated by application of the laws of Boyle and Charles.

Problems based on equations and involving gases may be solved *directly in terms of volume* by the application of the gram-molecular-volume relationship.

8.8. Molecular Weights of Liquids and Solids

The methods discussed thus far are suitable only for the determination of the molecular weights of gases. The same methods may be used in the case of liquids and solids that are volatile. All that one need do is to volatilize a sample of the liquid or solid and determine the weight of a known volume of the vapor at any convenient temperature and pressure. From these data, as has already been demonstrated, the molecular weight may be calculated. There are many liquids and solids, however, whose molecules undergo change with change in physical state; still others are essentially nonvolatile. In these instances, it is necessary to resort to other methods, such as those based upon a knowledge of the properties of solutions (Chap. 11).

8.9. Avogadro Number

On two occasions (Secs. 2.8 and 2.9) reference has been made to that number which represents (1) the number of atoms in 1 gram-atomic weight of an element, and (2) the number of molecules in 1 gram-molecular weight (or gram-molecular volume) of an elemental or compound substance. This number, 6.02×10^{23} (the Avogadro number) has been established *experimentally* by a wide variety of independent methods. The numerical value generally accepted as being the most accurate is that given above.

GENERAL EXERCISES

1. Distinguish clearly between absolute and relative weights of molecules.
2. State (*a*) Avogadro's law, (*b*) Gay-Lussac's law.
3. On the basis of the reaction between nitrogen and hydrogen (Fig. 53), develop an argument leading to the conclusion that the nitrogen molecule contains 2 atoms.
4. On the basis of Avogadro's law, show that the chlorine molecule is approximately two times as heavy as the hydrogen sulfide molecule.
5. If the rates of diffusion of two gases are measured accurately and the molecular weight of one is known, could these data be used to calculate the molecular weight of the other gas? Explain.

PROBLEMS

1. A 38-cc. sample of a certain gas at 23°C. and 774 mm. weighs 0.0937 g. (*a*) Calculate the molecular weight of this gas using hydrogen as a reference substance. (*b*) Make the same calculation using nitrogen as the reference substance. (*c*) Calculate the molecular weight of this gas through use of the gram-molecular-volume relationship.
2. If 120 cc. of a gas at 20°C. and 740 mm. weighs 0.2800 g., what is the molecular weight of the gas?
3. A gaseous compound consists of 82.65 per cent carbon and 17.35 per cent hydrogen; at S.T.P., 500 cc. of this gas weighs 1.3000 g. What is the formula of the compound?
4. A gaseous compound contains carbon and hydrogen only, the ratio by weight (C/H) being $^{12}/_{1}$. At 100°C. and 760 mm., 1 liter of the gas weighs 0.8491 g. What is the formula for this compound?
5. What volume (in liters) would be occupied by 1 g. of acetone (C_3H_6O) in the vapor state at 75°C. and 2 atm. pressure?
6. What is the volume (in liters) corresponding to 5.05 g. of nitrogen dioxide (NO_2) at S.T.P.?
7. If 1 ml. of liquid oxygen weighs 1.1400 g., what volume (in liters) of oxygen gas would result if one evaporated exactly 1 liter of liquid oxygen at S.T.P.?
8. Nitrogen gas is stored at 20°C. and 6 atm. in a steel cylinder having a capacity of 41.32 liters. How many grams of nitrogen are contained in the cylinder under these conditions?
9. A gaseous compound has the formula SiH_4. What is the weight (in grams) of 110 cc. of this gas at 25°C. and 750 mm.?
10. How many grams of carbon dioxide (CO_2) are contained in 150 liters of this gas at 100°C. and 756 mm.?
11. A sample of hydrogen bromide gas (HBr) occupies a volume of 0.3 liter at 20°C. and 740 mm. How many grams of the compound are contained in this sample?
12. How many liters of oxygen can be collected over mercury at 30°C. and 758 mm. by the complete decomposition of 200 g. of potassium chlorate?
13. The weight of 0.5 cc. of a certain gas at S.T.P. is 0.00198 g. Calculate the molecular weight of this gas.
14. If 0.1 g. of a gaseous compound occupies a volume of 48.9 cc. at 80°C. and 755 mm., what is the molecular weight of the compound?

15. What is the molecular weight of the gaseous compound, 0.342 g. of which occupies a volume of 65.5 cc. at 85°C. and 757 mm.?

16. If one wished to prepare potassium bromate ($KBrO_3$) by the reaction $6KOH + 3Br_2 \rightarrow KBrO_3 + 5KBr + 3H_2O$, how many liters of bromine gas (at 90°C. and 600 mm.) would be required to react with 1.5 g. of KOH?

17. Ten liters of carbon dioxide (CO_2) gas (at 25°C. and 770 mm.) were produced by the reaction $Na_2CO_3 + 2HCl \rightarrow CO_2 + H_2O + 2NaCl$. What fraction of a mole of Na_2CO_3 reacted?

18. Nitric oxide can be formed by the reaction

$$3Cu + 8HNO_3 \rightarrow 2NO + 4H_2O + 3Cu(NO_3)_2.$$

If the NO gas is collected at 0°C. and 750 mm., what volume could be formed if 1 g. of copper is used in the reaction? (Express answer in cubic centimeters.)

19. On the basis of the equation given in Prob. 18, calculate the weight of copper (in grams) required to produce 5 liters of nitric oxide, if the gas is collected at 15°C. and 740 mm.

SUGGESTED READING

See references at the end of Chap. 2.

CHAPTER 9

PREPARATION AND PROPERTIES OF HYDROGEN; RELATIVE ACTIVITY OF METALS

Hydrogen occupies a unique position among the elements in that it is the lightest known elemental substance. It occurs on the earth in tremendous quantities in combination with other elements and in like quantity (but in the uncombined condition) in the atmosphere of the sun. In 1766, Cavendish prepared hydrogen by a number of methods and studied many of its properties. He called it *inflammable air* and apparently failed to recognize it as an element. Somewhat later Lavoisier showed that this gas is one of the components of water and gave it the name *hydrogen*, which means "water former."

9.1. Laboratory Methods for the Preparation of Hydrogen

There are three convenient methods by means of which hydrogen is usually prepared for small-scale laboratory use.

Preparation from Metals and Acids. Acids are substances that consist of hydrogen combined with one or more nonmetals, *e.g.*, hydrochloric acid (HCl) and sulfuric acid (H_2SO_4). When certain acids are allowed to react with certain of the metals, hydrogen gas is liberated and there are formed also compounds known as *salts*. In these salts, the metals are found to be combined with the nonmetals which were originally combined with hydrogen in the acid used. Reactions that serve to illustrate this method of preparation are represented by the following equations:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

$$2Na + 2HCl \rightarrow 2NaCl + H_2$$

$$2Al + 2H_3PO_4 \rightarrow 2AlPO_4 + 3H_2$$

Phosphoric acid

$$Mg + 2HC_2H_3O_2 \rightarrow Mg(C_2H_3O_2)_2 + H_2$$

Acetic acid

Not all acids can be used in the preparation of hydrogen. Nitric acid and *concentrated* sulfuric acid react with metals to form salts and prod-

ucts other than hydrogen. Neither can all metals be used. Some metals react with acids so slowly that their use would be inadvisable; other metals are incapable of reaction with acids. Zinc and hydrochloric acid or dilute sulfuric acid are the substances most often employed in the laboratory for the preparation of hydrogen (Fig. 56).

With any given acid, the reactions with different metals do not all occur at the same rate. Some metals react vigorously, others somewhat more slowly, and still others react only extremely slowly or not at all.

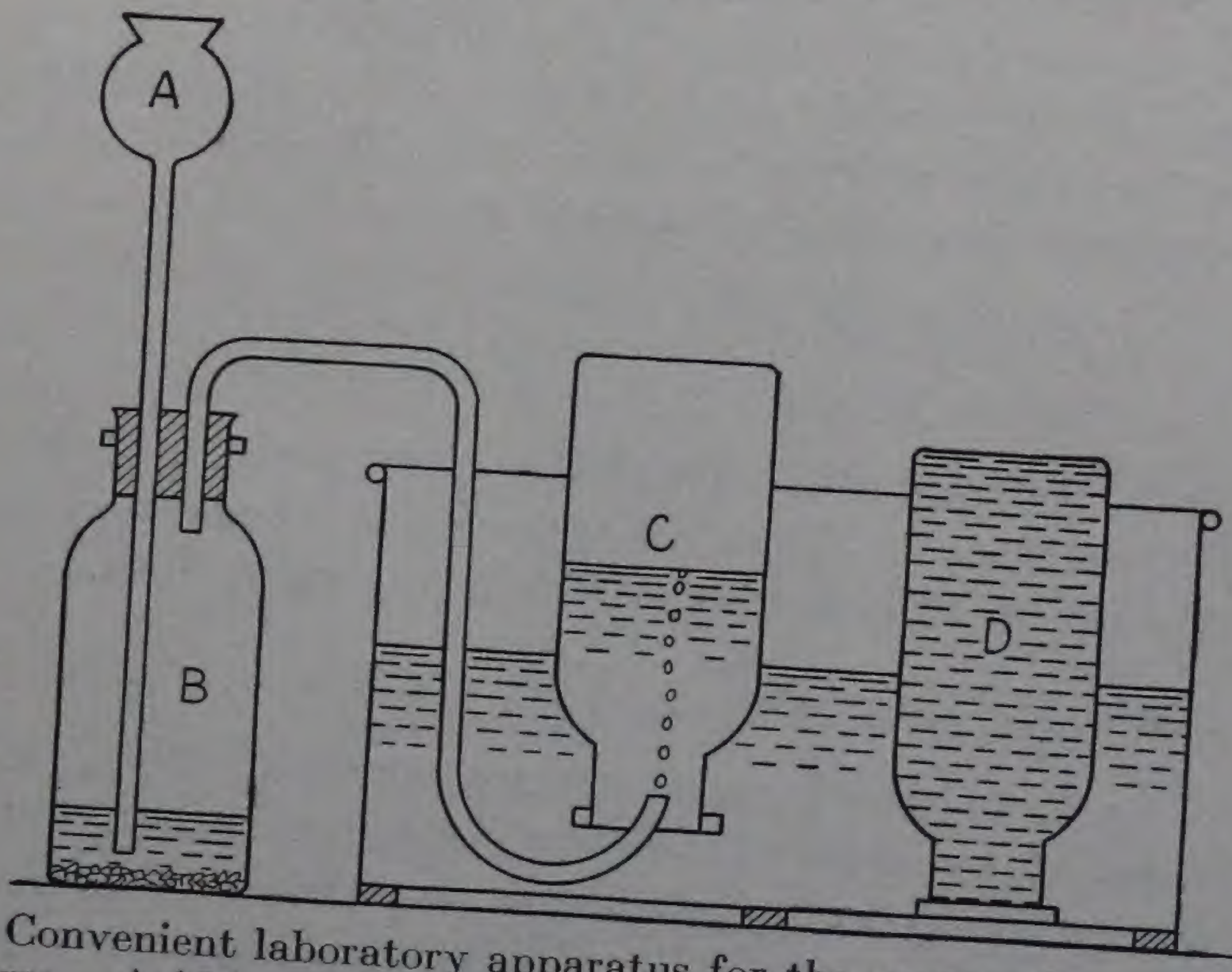

FIG. 56. Convenient laboratory apparatus for the preparation and collection of hydrogen gas. Acid is added through the thistle tube, *A*, to the metal contained in bottle *B*. The hydrogen liberated is collected by displacement of water contained in bottles *C* and *D*.

Preparation from Metals and Water. Just as certain metals are capable of displacing the hydrogen from certain acids, so hydrogen may be displaced from water under suitable conditions. At ordinary temperatures, the metal sodium displaces hydrogen from cold water in a reaction that is extremely vigorous.

$$2Na + 2HOH \rightarrow 2NaOH + H_2$$

The other product in reactions of this type is known as a *base* and consists of a metal in combination with hydrogen and oxygen.

If the metal magnesium is allowed to react with cold water, the reaction is very slow. With hot water, however, hydrogen is liberated at an appreciable rate.

$$Mg + 2HOH \rightarrow Mg(OH)_2 + H_2$$

The metal iron does not react either with cold or hot water at an appreciable rate. With steam, the reaction proceeds at a rate such that this may be used in the laboratory preparation (or commercial production) of hydrogen.

$$3Fe + 4HOH \rightarrow Fe_3O_4 + 4H_2$$

In this particular reaction, an oxide and not a hydroxide is formed as a by-product.

It should be emphasized that all metals do not react with water and that those which react do so at markedly different rates.

Preparation from Metals and Bases. A few of the metals, such as aluminum and zinc, react with bases with liberation of hydrogen accompanied by the formation of salts.

$$Zn + 2NaOH \rightarrow (NaO)_2Zn + H_2$$
$$2Al + 6NaOH \rightarrow 2(NaO)_3Al + 3H_2$$

Here, as before, the reactions are of the same general character but occur at different rates. Of the three methods for the preparation of hydrogen, the action of bases on metals is the least used.

9.2. Order of Activity of Metals

When the reactions of a large number of metals with (1) acids, (2) water, (3) bases, (4) oxygen, (5) other elements, and (6) other compounds are investigated in the laboratory, it is found that the various metals react at different rates. That is, these metals seem to exhibit different tendencies toward participation in chemical changes. Measurement of the rates at which metals react with various substances (*e.g.*, acids) makes possible the establishment of a definite "order of activity" such as that given in Table 10. In this table the metals are listed in *decreasing* order of activity, *i.e.*, the higher the metal in this series the greater is its activity or tendency to react. For the sake of simplicity many of the less common metals have been omitted, but such a list could be established readily to include all the known metals. The order in which the metals are listed in Table 10 depends upon their respective tendencies toward the loss of electrons. Of the metals included, potassium shows the greatest tendency to lose the 1 electron from its outermost shell; gold the least tendency to do so. Barium atoms lose electrons less readily than potassium atoms, but more readily than calcium atoms. Since loss of electrons constitutes oxidation, the order in which metals are listed in Table 10 reflects their relative ease of oxidation, and consequently their relative effectiveness as

reducing agents. Thus, magnesium is a better reducing agent than zinc because magnesium atoms lose electrons more readily, and it is these electrons that are gained in accompanying reduction reactions. From this it follows that the strongest reducing agents (weakest oxidizing agents) are those metals listed toward the top of Table 10. Similarly, the weakest reducing agents (strongest oxidizing agents) found among the metals are those listed toward the bottom of Table 10.

TABLE 10

ORDER OF ACTIVITY OF METALS

Potassium
Barium
Calcium
Sodium
Magnesium
Aluminum
Manganese
Zinc
Chromium
Iron
Cadmium
Nickel
Tin
Lead
Hydrogen
Bismuth
Copper
Silver
Mercury
Platinum
Gold

The inclusion of hydrogen (a nonmetal) in Table 10 is worthy of particular attention. Even if there were no better reason, its inclusion could easily be justified because in its reactions hydrogen exhibits many similarities to the metals. Hydrogen is included also because it provides a line of demarcation between those metals which will and those which will not react with acids to liberate hydrogen. In this connection, the following generalizations may be made:

1. Metals above hydrogen react with acids (other than ones such as nitric and concentrated sulfuric) to form hydrogen and a salt.
2. Metals below hydrogen do not react with acids with liberation of hydrogen.
3. Metals below hydrogen and above platinum react with acids such as nitric and concentrated sulfuric to form salts and products other than hydrogen.

4. Platinum and gold do not react with pure acids of any kind, but these metals are slowly attacked by *aqua regia*. (This latter reagent consists of a mixture of concentrated nitric and concentrated hydrochloric acids. The reactions with platinum and gold depend upon the presence of elemental chlorine, which is formed by a reaction between the two concentrated acids.)

9.3. Radicals

The equations written to represent the reactions by means of which hydrogen may be prepared present some problems that require further comment. In the equation,

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

a portion, SO_4, of the formula for the acid is also a part of the formula for the salt ($ZnSO_4$). It appears that this particular group of atoms was unaltered in the course of the reaction. Inspection of the other equations reveals the presence of several groups of atoms which behave similarly, *e.g.*, PO_4, $C_2H_3O_2$, OH, and NaO. Such groups of atoms are known as *radicals*. **A radical is defined as a group of atoms that behaves as an unaltered unit in a chemical reaction.** Where different radicals or two or more of the same kind of radical are present in the formula of a compound, these radicals are usually enclosed in parentheses. It should not be inferred that a group of atoms that constitutes a radical in one reaction must always behave as a unit. All of the common radicals can be disrupted by suitable kinds of chemical attack.

9.4. Valence of Common Elements and Radicals

Although, as pointed out in Sec. 4.11, the concept of valence is quite arbitrary unless considered in relation to the nature of the chemical bonds involved, this arbitrary concept is nevertheless one of convenience. Chemical formulas and equations may be written even though little or nothing is known about the ionic or covalent character of the chemical combinations represented. On the basis of only a limited amount of information concerning a few simple compounds, the formulas for many other compounds may be deduced.

Suppose, for example, that one wished to write the correct formula for magnesium nitride, Mg_xN_y, where x and y represent the numbers of magnesium and nitrogen atoms in the molecule. In the covalent NH_3 molecule, the nitrogen atom forms three covalent bonds with 3 hydrogen atoms, and the valence of nitrogen is therefore 3. Since the nitro-

gen atom has 5 electrons in its outermost shell, it tends to gain 3 electrons or to share three pairs of electrons so as to achieve an inert-gas structure. Similarly, magnesium forms a compound having the formula $MgCl_2$, and this is an ionic compound formed when the magnesium atom loses the 2 electrons in the outermost shell and these 2 electrons are gained by the 2 chlorine atoms. Consequently, one reaches the conclusion that the valence of magnesium is 2. From this it follows that if, in magnesium nitride, 1 atom of magnesium loses 2 electrons, this is one less than the number required by the nitrogen

TABLE 11
VALENCE OF COMMON ELEMENTS

Univalent (valence = 1)	Divalent (valence = 2)	Trivalent (valence = 3)	Tetravalent (valence = 4)
Metals			
Na K Ag Cu Hg	Cd Mg Ca Mn Ba Hg Cu Sn Fe Zn Pb	Al Bi Fe Cr	Sn Pb
Nonmetals			
Br Cl F I H	O S	N P B	Si C

atom. If, however, 3 magnesium atoms lose a total of 6 electrons (2 each), this is the number that can be gained by 2 atoms of nitrogen (3 each). Accordingly, the correct simplest formula for magnesium nitride must be Mg_3N_2. The same conclusion is reached by the same line of reasoning in terms of pairs of electrons shared rather than in terms of electrons lost and gained.

For reference, the valences usually exhibited by the more common metals and nonmetals are given in Table 11. Elements that commonly exhibit more than one valence are listed in more than one column. The names, formulas, and valences of the common radicals are listed in Table 12.

Without any reference whatever to the nature of the bonds involved, the information given in Tables 11 and 12 leads to the conclusion that

the formula for chromium bromide must be $CrBr_3$, the formula for copper oxide may be either CuO or Cu_2O, that for calcium acetate is $Ca(C_2H_3O_2)_2$, etc.

TABLE 12
COMMON RADICALS

Ion	Formula	Valence
Ammonium	NH_4^+	1
Hydroxyl (or hydroxide)	OH^-	1
Nitrate	NO_3^-	1
Nitrite	NO_2^-	1
Acetate	$C_2H_3O_2^-$	1
Chlorate	ClO_3^-	1
Chlorite	ClO_2^-	1
Hypochlorite	ClO^-	1
Sulfate	$SO_4^=$	2
Sulfite	$SO_3^=$	2
Carbonate	$CO_3^=$	2
Phosphate	$PO_4^{\equiv}$	3
Phosphite	$PO_3^{\equiv}$	3

The problem of writing the equation for the reaction between cadmium and phosphoric acid serves as an additional illustration.

$$Cd + H_3PO_4 \rightarrow Cd_x(PO_4)_y + H_2$$

The valence of Cd is 2, that of the PO_4 radical is 3; hence, the formula for the salt, cadmium phosphate, must be $Cd_3(PO_4)_2$, and

$$Cd + H_3PO_4 \rightarrow Cd_3(PO_4)_2 + H_2$$

The formula $Cd_3(PO_4)_2$ requires that at least 3 atoms of Cd and 2 molecules of H_3PO_4 be used,

$$3Cd + 2H_3PO_4 \rightarrow Cd_3(PO_4)_2 + H_2$$

and the use of $2H_3PO_4$ provides a total of 6 atoms of hydrogen or 3 molecules, $3H_2$. The complete and balanced equation therefore is

$$3Cd + 2H_3PO_4 \rightarrow Cd_3(PO_4)_2 + 3H_2$$

9.5. Determination of Equivalent Weights of Metals

Measurement of the volumes of hydrogen evolved during reactions between metals and acids provides a simple and convenient means of determining equivalent weights of metals. If, for example, 1 gram-

atomic weight of sodium (22.997 g.), 1 gram-atomic weight of zinc (65.38 g.), and 1 gram-atomic weight of aluminum (26.97 g.) are each treated separately with an excess of dilute sulfuric acid, hydrogen is evolved in each case. The relative volumes of hydrogen (corrected to standard conditions) liberated by gram-atomic weights of the three metals are represented by Fig. 57.

It is found that 1 gram-atomic weight of sodium displaces 1 gram-atomic weight of hydrogen (1.008 g.). This is 1 equivalent weight of

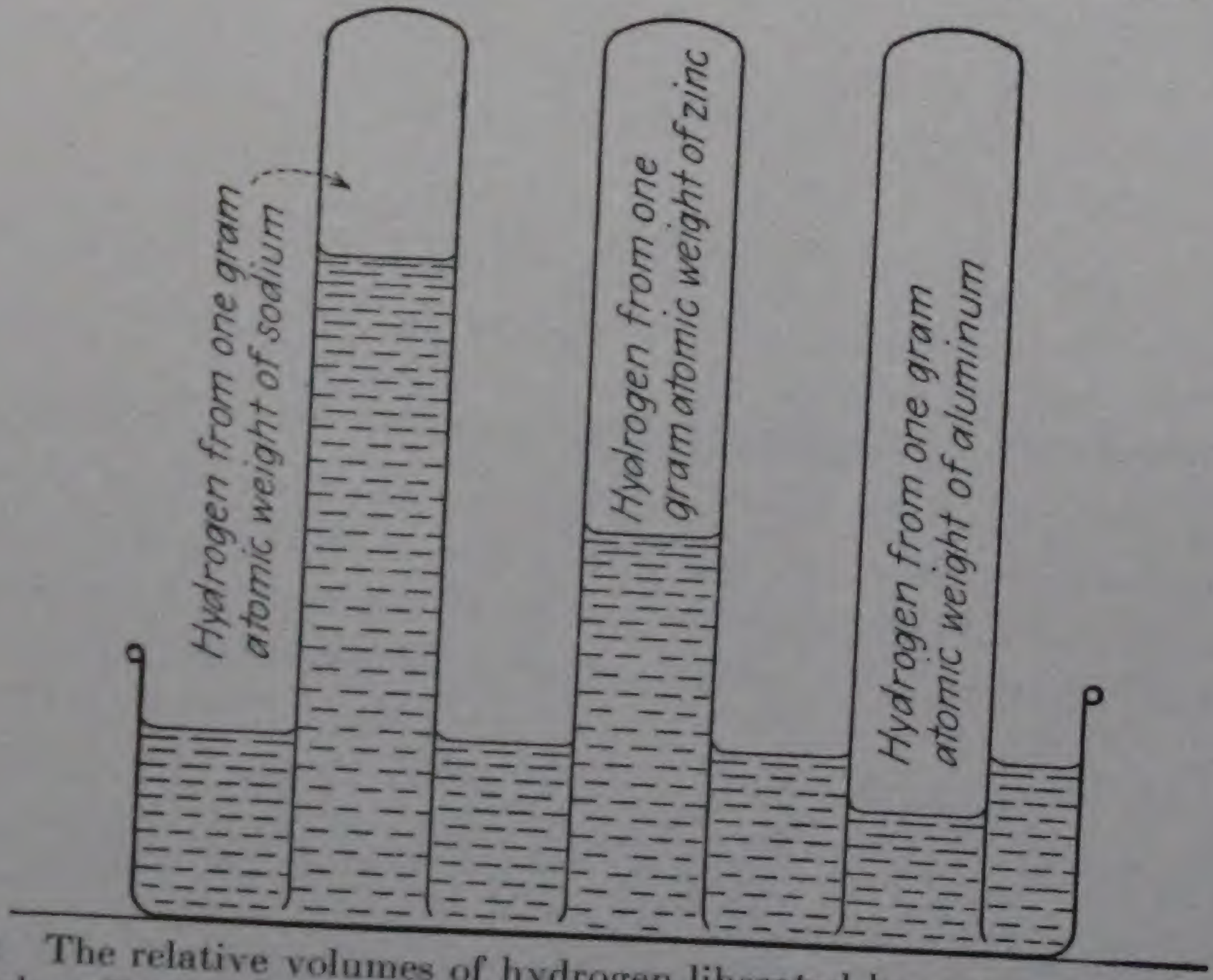
Hydrogen from one gram atomic weight of sodium
Hydrogen from one gram atomic weight of zinc
Hydrogen from one gram atomic weight of aluminum

FIG. 57. The relative volumes of hydrogen liberated by gram-atomic weights of the metals sodium, zinc, and aluminum.

hydrogen, *i.e.*, that equivalent to 8 g. of oxygen (Sec. 2.2), and consequently the equivalent weight of sodium must be 22.997 g. In the reaction with the acid, each sodium atom loses the 1 electron in its outermost shell, and the equivalent weight of sodium is therefore seen to be that associated with a 1-electron change. One gram-atomic weight of zinc liberates twice as much hydrogen (Fig. 57) as one gram-atomic weight of sodium. That is, 1 gram-atomic weight of zinc liberates 2.016 g., or 2 equivalents, of hydrogen, and this corresponds to a 2-electron change. Hence, the equivalent weight of zinc must be $65.38/2 = 32.69$ g. One gram-atomic weight of aluminum liberates three gram-atomic weights of hydrogen, and the equivalent weight of aluminum is $26.97/3 = 8.99$ g. These illustrations should also make evident the fact that the equivalent weight is equal to the atomic weight divided by the valence.

In order to determine equivalent weights of metals in the laboratory by means of reactions between metals and acids, it is necessary only to measure the volume of hydrogen liberated at known temperature and barometric pressure by a known weight of the metal in question. For example, 0.1 g. of aluminum was found to react with excess sulfuric acid to liberate a volume of hydrogen which, when corrected to standard conditions, amounted to 124.6 c.c. By definition, the equivalent weight of aluminum is that which would liberate 1 *gram-atomic* weight of hydrogen at standard conditions, and this is 11.2 liters (since 1 *gram-molecular* weight of hydrogen occupies a volume of 22.4 liters at standard conditions). Hence, by simple proportion,

$$\text{Equiv. wt. of Al} = \frac{11{,}200 \times 0.1}{124.6}$$

$$= 8.99 \text{ g.}$$

9.6. Commercial Methods for the Preparation of Hydrogen

Of the methods given for the laboratory preparation of hydrogen, only the reaction between iron and steam is suitable for industrial application, and it is so used only to a limited extent. Some hydrogen is produced commercially by the catalytic decomposition of ammonia.

$$2NH_3 \rightarrow N_2 + 3H_2$$

and some is obtained as a by-product of the production of chlorine, alcohols, and other chemicals.

Bosch Process. The chief commercial method for the production of hydrogen is known as the *Bosch process* and involves the reaction between steam and hot carbon.

$$C + H_2O \rightarrow CO + H_2$$

The mixture of carbon monoxide and hydrogen is known as *water gas.* The carbon monoxide then reacts with additional steam to form carbon dioxide and more hydrogen.

$$CO + H_2O \rightarrow CO_2 + H_2$$

The separation of the CO_2 and H_2 is accomplished by dissolving the CO_2 in water under high pressures, under which conditions only a very small quantity of the hydrogen is dissolved.

Preparation from Methane. A method similar to the Bosch process is that which depends upon the reaction between methane (CH_4), which is the chief component of natural gas, and steam,

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
$$CO + H_2O \rightarrow CO_2 + H_2$$

The CO_2 and H_2 are separated by the same method as that described in connection with the Bosch process. Hydrogen is also produced commercially by decomposing methane in contact with refractory bricks at 1000° to 1100°C.

Preparation by the Electrolysis of Water. It was pointed out in Sec. 5.1 that the decomposition of water by means of an electric current provides a means of securing oxygen gas on a commercial scale. At the same time hydrogen gas is liberated.

$$2H_2O \rightarrow 2H_2 + O_2$$

By suitable arrangement of apparatus the two gases may be collected separately. Although this method is not so extensively used as the two preceding ones, it is of interest because it permits the simultaneous production of two common and important gases.

9.7. Physical Properties of Hydrogen

Hydrogen is a colorless, odorless, tasteless gas which is soluble in water only to the extent of 1.78 cc. per 100 cc. of water at 20°C. It is the lightest known gas, having a density of 0.0899 g. per liter at S.T.P., and is nearly 14.5 times lighter than air. Other significant physical properties of hydrogen are critical temperature = −239.9°C., boiling temperature = −252.78°C., and freezing temperature = −259.2°C.

9.8. Chemical Behavior of Hydrogen

Under suitable conditions, hydrogen combines with all the nonmetals except the inert gases and with many of the metals as well. The compounds with the metals are called *hydrides;* those with the nonmetals are given other names. Most reactions between hydrogen and the elements require elevated temperatures.

$$2Na + H_2 \rightarrow \underset{\text{Sodium hydride}}{2NaH}$$

$$Ca + H_2 \rightarrow \underset{\text{Calcium hydride}}{CaH_2}$$

$$S + H_2 \rightarrow \underset{\text{Hydrogen sulfide}}{H_2S}$$

$$2P + 3H_2 \rightarrow \underset{\text{Phosphine}}{2PH_3}$$

Of particular importance is the formation of water by the direct union of hydrogen and oxygen. This reaction does not occur at all at ordinary temperatures but occurs slowly at 500°C. and almost instantaneously at 700°. This reaction is catalyzed by finely divided platinum (Pt), palladium (Pd), iron, iron oxide, etc. These and other catalysts have the property of absorbing (or adsorbing) huge quantities of hydrogen on their surfaces, and the catalytic action probably is due to the resulting localized increase in the concentration of hydrogen with resultant increase in the rate of combination with oxygen at the surface of the catalyst. For example, 1 volume of powdered palladium metal is capable of absorbing about 800 volumes of hydrogen at ordinary temperatures.

When two parts by volume of hydrogen and one part by volume of oxygen are brought together, the mixture may be caused to react with explosive violence by a flame or an electric spark. This behavior is the cause of numerous industrial accidents and of explosions suffered by balloons and other lighter-than-air craft filled with hydrogen. Such craft are subject to the hazard of explosions due to ignition of an explosive mixture of hydrogen and air by electric sparks, lightning, flames, or incendiary bullets. Pure hydrogen burns with a colorless but extremely hot flame.

Reducing Action of Hydrogen. At suitably elevated temperatures, hydrogen reacts with many compounds to remove and combine with one or more of the elements contained in the compound. At high temperatures hydrogen removes and unites with the oxygen contained in the oxides of certain metals (Fig. 58).

$$CuO + H_2 \rightarrow Cu + H_2O$$

$$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O$$

These changes are typical oxidation-reduction reactions, and the metal oxides are said to be *reduced*.

It is enlightening to consider, in terms of the order of activity of metals, the ease with which oxygen can be removed from oxides of the metals. Starting at the bottom of the list (Table 10), oxygen may be removed readily from the oxides of gold, platinum, mercury, and silver merely by the application of heat. From silver to and including iron, the removal of oxygen from the corresponding oxides becomes increasingly difficult but may be accomplished by reduction with hydrogen. The oxides of the metals above iron are still more stable (resistant to decomposition), and the removal of oxygen from these oxides requires still more vigorous modes of chemical attack. From all this it may be

concluded that the metals that stand highest in the order of activity form, in general, the most stable compounds.

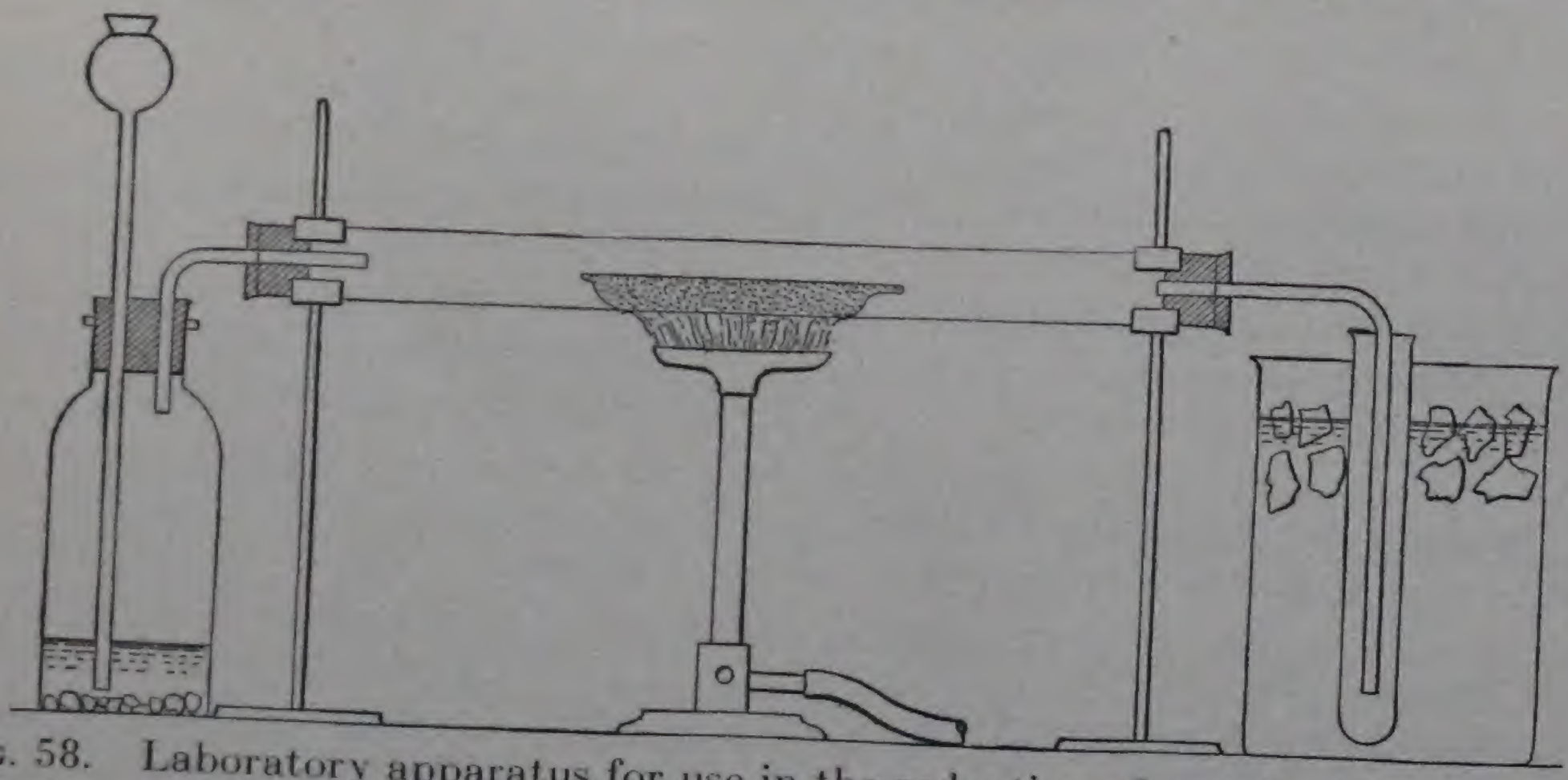

FIG. 58. Laboratory apparatus for use in the reduction of metal oxides by means of hydrogen. The oxide to be reduced is placed in a porcelain boat contained in a glass tube which is connected to the hydrogen generator shown on the left. Water formed in the reaction may be condensed in the test tube cooled in an ice bath.

9.9. Uses of Hydrogen

In the United States alone the annual consumption of hydrogen in the various chemical and metallurgical industries reaches enormous proportions. Large quantities of hydrogen are used in the manufacture of ammonia, which in turn is converted into fertilizers and explosives. Fat substitutes are produced by the "hydrogenation" of liquid oils of animal and vegetable origin. From 1000 to 5000 cu. ft. of hydrogen is required to convert 1 ton of cottonseed oil to a semisolid mass which may be used as a substitute for lard or in the manufacture of soap. Another large-scale use of hydrogen is the hydrogenation of coal. In this process, a part of the coal is changed to a light oil from which gasoline and lubricating oils may be obtained. Hydrogen is used in the production of methyl alcohol ("wood alcohol") by the catalyzed reaction between hydrogen and carbon monoxide. Other applications include the use of hydrogen as a fuel in the atomic-hydrogen torch and as a reducing agent in the commercial production of certain metals. Despite the danger of explosions, hydrogen is still used for the inflation of balloons and dirigibles in those countries to which helium is not available.

GENERAL EXERCISES

1. Write equations representing three laboratory methods and three commercial methods for the preparation of hydrogen.

2. Knowing that both CO and H_2 are only sparingly soluble in water, suggest a method whereby hydrogen could be separated from carbon monoxide.

3. Write formulas for the simple binary compounds formed by the direct union of the following pairs of elements:

(*a*) Potassium and sulfur
(*b*) Barium and fluorine
(*c*) Aluminum and iodine
(*d*) Bismuth and nitrogen
(*e*) Silver and phosphorus
(*f*) Boron and bromine
(*g*) Potassium and chlorine
(*h*) Silicon and bromine
(*i*) Sodium and oxygen
(*j*) Bismuth and sulfur
(*k*) Barium and phosphorus
(*l*) Cadmium and iodine

4. Inspect the following formulas to determine which ones are incorrectly written, and write the corresponding correct formulas:

(*a*) Bismuth fluoride, BiF_3
(*b*) Aluminum phosphate, $Al_3(PO_4)_2$
(*c*) Zinc chloride, ZnCl
(*d*) Lead acetate, $Pb(C_2H_3O_2)_2$
(*e*) Calcium nitrite, $Ca(NO_2)_2$
(*f*) Aluminum hydroxide, $Al(OH)_3$
(*g*) Iron phosphite, $Fe_3(PO_3)$
(*h*) Cadmium sulfide, CdS
(*i*) Potassium chlorate, $KClO_3$
(*j*) Chromium nitrate, $Cr(NO_3)_3$

5. What is the valence of each of the radicals (enclosed in parentheses) in the following formulas: (*a*) $Na(ClO)$, (*b*) $H(MnO_4)$, (*c*) $K_3(PO_4)$, (*d*) $Na_2(B_4O_7)$, (*e*) $Ca(S_2O_3)$, (*f*) $Ba_3(BO_3)_2$, (*g*) $(ZrO)(NO_3)_2$, (*h*) $(UO_2)Cl_2$, (*i*) $(NH_4)_2(SO_4)$?

6. If the valence of H = 1, F = 1, and O = 2, deduce the valences of the elements in the following compounds: (*a*) H_2S, (*b*) NH_3, (*c*) CrF_3, (*d*) HBr, (*e*) B_2O_3, (*f*) BiI_3, (*g*) Fe_2S_3, (*h*) Al_2S_3, (*i*) $CrCl_3$, (*j*) HgCl, (*k*) $MnBr_3$, (*l*) $ThCl_4$, (*m*) SiH_2Cl_2.

7. The following reactions are suggested as means of producing metals by the thermal decomposition of oxides, or the reduction of oxides by means of hydrogen. Write equations for those cases in which the suggested reaction will occur.

(*a*) Ag_2O + heat
(*b*) ZnO + heat
(*c*) NiO + hydrogen
(*d*) Bi_2O_3 + hydrogen
(*e*) Al_2O_3 + hydrogen
(*f*) CaO + heat

8. Each of the following pairs of substances represents a combination of metal and acid for use in the preparation of hydrogen. For those cases in which the formation is possible, write equations for the reactions.

(*a*) Tin + hydrochloric acid
(*b*) Magnesium + acetic acid
(*c*) Copper + phosphoric acid
(*d*) Calcium + hydrochloric acid
(*e*) Manganese + nitric acid
(*f*) Cadmium + acetic acid

9. If magnesium reacts with hot water, why is it possible to use magnesium-aluminum alloys in airplane construction?

PROBLEMS

1. Calculate the weight of tin required to produce 22 tons of hydrogen gas.

2. (*a*) What volume of hydrogen (in cubic centimeters, at S.T.P.) will be produced if 0.01 gram-atomic weight of zinc is dissolved in dilute sulfuric acid? (*b*) What volume would this hydrogen occupy if it had been collected over mercury in a laboratory in which the temperature was 30°C. and the barometric pressure was 730 mm.?

3. (*a*) How many grams of sulfuric acid are required to dissolve exactly 1 g. of iron? (*b*) What volume of hydrogen (in cubic centimeters at S.T.P.) is liberated during the course of this reaction?

4. If hydrogen is to be produced by the reaction between magnesium and water, what weight of water (in grams) will be consumed in the production of 89.6 liters of hydrogen (measured at S.T.P.)?

5. Calculate the weight of lead that will result if 10 lb. of lead oxide is reduced by means of hydrogen gas.

6. The metal tungsten is produced commercially by reducing the oxide, WO_3, with hydrogen gas; the other reaction product is water. Calculate the weight of tungsten that could be produced by the use of 1 ton of hydrogen.

7. How many liters of hydrogen gas at S.T.P. would be required to reduce 6.38 g. of iron oxide in accordance with the equation $Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O$?

8. When 1.338 g. of a certain metal was dissolved in dilute hydrochloric acid, 266.6 cc. of hydrogen (at S.T.P.) was liberated. Calculate the equivalent weight of this metal.

9. Treatment of 0.8 g. of a metal with excess acid gave hydrogen, which was collected over water in a laboratory in which the temperature was 27°C. and the barometric pressure was 756.7 mm. If the volume of gas collected was 500 cc., what is the equivalent weight of the metal?

10. The reaction between 0.01 g. of potassium and water gave 3.24 cc. of hydrogen when the gas was collected over water at 24°C. and 750 mm. Calculate the equivalent weight of potassium.

11. A balloon was partially inflated with 1000 cu. ft. of hydrogen at 25°C. and 750 mm. To what volume would the balloon expand if it were allowed to ascend into a region where the temperature is 10°C. and the pressure 75 mm.?

SUGGESTED READING

Journal of Chemical Education

Alexander and Byers, Hydrogen from Iron and Water, **9**, 916 (1932).
Bartlett, Atomic Hydrogen Flames, **4**, 39 (1927).

Industrial and Engineering Chemistry

Kanolt and Cook, Production of Pure Hydrogen for Liquefaction, **17**, 183 (1925).
Claude, The Manufacture of Hydrogen by the Partial Liquefaction of Water Gas and Coke-oven Gas, **14**, 1113 (1922).
Karzhavin, Hydrogen from Natural Gas, **28**, 1042 (1936).
Brownlie, Bulk Production of Hydrogen, **30**, 1139 (1938).

CHAPTER 10

SOLUTIONS

The chemical changes described in detail or used as illustrations up to this point have been concerned for the greater part with pure gases, liquids, or solids. Hereafter, greater emphasis is placed upon reactions involving mixtures, but mixtures of the particular variety known as *solutions*. The manufacture of many useful chemical products and the great majority of the more important types of chemical change involve solutions either directly or indirectly.

10.1. Nature of Solutions

Everyone is familiar with the fact that some liquids have the ability to wet the surfaces of solids. This wetting effect is the result of an attraction between the molecules of the liquid and those of the solid. In many cases, these attractive forces succeed in dislodging single molecules (or larger particles) of the solid and in surrounding the dislodged molecules completely by molecules of the liquid. Under these circumstances, the solid is said to *dissolve* in the liquid, and the resulting mixture of solid dissolved in liquid is called a *solution*.

If the dissolved substance exists in the solution in the form of single molecules or very small clusters or groups of molecules uniformly distributed throughout the body of the liquid, the mixture is perfectly homogeneous and the dissolved particles show no tendency to settle out under the influence of gravity. A mixture of this character is known as a *true solution*. If, however, the particles consist of large clusters or groups of molecules, the resulting mixture is perfectly homogeneous, the particles show at least a limited tendency to settle under the influence of gravity, and the mixture is said to be a *colloid*. There is yet another possibility. Suppose that the particles are of such size (very large groups of molecules—particles visible to the unaided eye) that the mixture is obviously heterogeneous and the particles can be made to remain distributed throughout the liquid only by continuous stirring. Under these conditions the mixture is properly described as a *suspension*. The distinction, then, between true solutions, colloids, and suspensions is largely one of relative particle size.

A clear distinction must also be drawn between solutions and compounds. It has been established already that compounds are substances having absolutely definite composition, and this is certainly not true of solutions. One may dissolve 1 g., 10 g., or 100 g. of cane sugar in 1 liter of water, and in each case there is formed a true solution. The composition of a true chemical compound, however, is not subject to any such variations. Accordingly, it is seen that solutions differ from compounds in that the composition of solutions is variable.

10.2. Composition of Solutions

In view of the foregoing ideas concerning the nature of solutions, **a solution may be defined as a homogeneous mixture the composition of which may be varied between certain definite limits.** Every solution must consist of at least two components: a *solute* and a *solvent*. These two components are usually designated in terms of the relative quantities involved; the component present in larger quantity is usually called the solvent. For example, if a solution consists of a homogeneous mixture of 10 g. of ordinary table salt and 100 g. of water, the salt is the solute and the water is the solvent. If, however, a homogeneous mixture consisted of 100 g. of water and 100 g. of alcohol, a clear distinction between solute and solvent could not be made except on some wholly arbitrary basis.

10.3. Classification of Solutions on the Basis of the Physical State of the Solute and Solvent

Unless some thought is given to the matter, one is likely to get into the habit of thinking of solutions only in terms of solutions of solids in liquids. Although it is true that most common solutions are of this variety, there are eight other possible types of mixtures. The nine types, together with suitable examples, in the cases of those which frequently exist as true solutions include:

1. *Solutions of Gases in Gases.* Example: air or any other homogeneous mixture of gases.
2. *Solutions of Gases in Liquids.* Example: "carbonated" soft drinks, which consist of carbon dioxide gas (and other solutes) dissolved in water.
3. *Solutions of Gases in Solids.* Example: the absorption of hydrogen by palladium (Sec. 9.8) may be looked upon as a situation in which a gas is dissolved in a solid.
4. *Solutions of Liquids in Liquids.* Example: a mixture of alcohol and water.

5. *Solutions of Liquids in Solids.* Example: the liquid metal mercury forms solutions with certain solid metals such as gold.

6. *Solutions of Solids in Liquids.* Example: sugar dissolved in water, or any other of the many familiar examples of this the most common type of solution.

7. *Solutions of Solids in Solids.* Example: the alloy known as brass consists of a *solid solution* of zinc in copper.

8. *Mixtures of Liquids and Gases.*

9. *Mixtures of Solids and Gases.*

Any substance that dissolves in a given solvent is said to be *soluble* in that solvent.

10.4. Classification of Solutions in Terms of the Quantity of Solute

In speaking of the concentration of solutes present in solutions (*i.e.*, the quantity of solute per unit volume of solution) the chemist uses certain terms that are somewhat indefinite but nevertheless convey real meanings. Two purely relative designations are the terms *concentrated* and *dilute*. Concentrated solutions are understood to be ones that are relatively rich in solute as compared with dilute solutions, in which the concentration of solute is relatively small. In an effort to qualify these already indefinite terms, the chemist employs numerous variations. Thus, one speaks of "highly concentrated," "very dilute," "moderately dilute" solutions, etc.

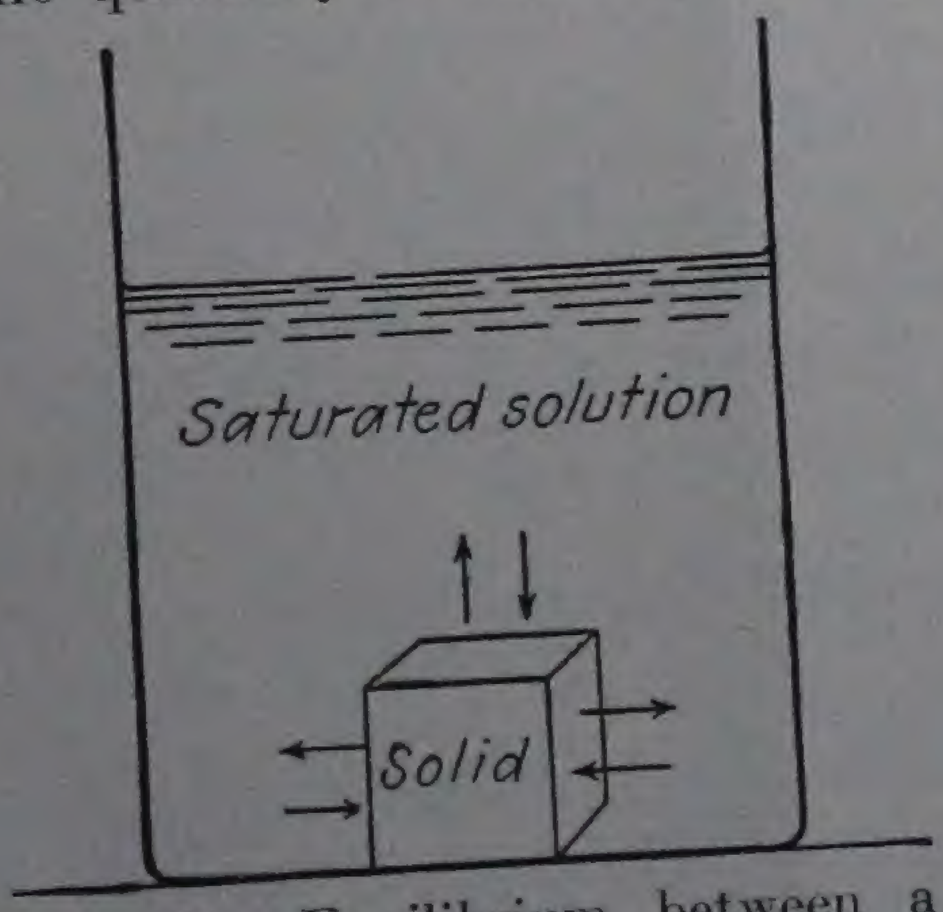

FIG. 59. Equilibrium between a solid and a saturated solution.

Saturated Solutions. If a large cube of sugar is allowed to stand in the presence of a quantity of water insufficient to dissolve all of the sugar, molecules of the solid sugar go into solution and distribute themselves uniformly throughout the body of the liquid. At any given temperature, this process continues, and as the concentration of sugar molecules in solution increases, some of these molecules leave the solution and return to the solid. In time, the rate at which molecules are leaving the solution and returning to the solid becomes equal to the rate at which molecules are leaving the solid and entering the solution

(Fig. 59). In other words, a condition of dynamic equilibrium becomes established, and under these conditions the solution is said to be *saturated*. Accordingly, **a saturated solution is one which is in equilibrium with an excess of the undissolved solute.**

It is easy to prove that a condition of dynamic equilibrium exists in a saturated solution. If a broken or otherwise imperfect crystal is suspended (by means of a fine wire) in a saturated solution in which the solute is of the same composition as the crystal, the solution remains saturated and the total weight of the crystal does not change. In time, however, the imperfection in the crystal tends to be repaired. That is, solute molecules leave from any or all surfaces of the crystal but return from the solution to the crystal primarily in the region where the imperfection exists.

Standard Solutions. In studying the properties of solutions and in carrying out chemical reactions involving solutions, it is frequently necessary to use solutions containing definite known quantities of solute. Any solution of known concentration is classed as a *standard solution*. There are several different kinds of standard solutions in common use, *e.g.*, *molar* and *molal* solutions.

A molar solution is one which contains one gram-molecular weight of a solute dissolved in enough solvent to make exactly one liter of solution. For example, if 1 gram-molecular weight (1 mole) of alcohol (C_2H_6O) (46 g.) is dissolved in enough water to make 1 liter of solution, the resulting solution is *one molar* (1*M*). If 2 moles ($2 \times 46 = 92$ g.) are dissolved in enough water to make 1 liter of solution, this solution is *two molar* (2 *M*), etc. Similarly, 1 liter of solution containing $\frac{1}{10}$ mole of alcohol ($\frac{1}{10} \times 46 = 4.6$ g.) is said to be *one-tenth molar* (0.1 *M*). Solutions prepared on the basis of molarity are particularly useful in the study of those properties of solutions which depend upon the number of molecules contained in a given volume of solution. One liter of a 1 *M* solution of any solute contains, of course, 6.02×10^{23} molecules of solute; a 0.5 *M* solution contains just one-half this number of molecules, etc.

A molal solution is one which consists of one gram-molecular weight of solute dissolved in 1000 grams of solvent. Since in dilute solutions 1000 g. of solvent and 1 liter of a water solution are not greatly different, a one-tenth molal (0.1 *m*) and a one-tenth molar (0.1 *M*) solution may be practically identical. On the other hand, one molal and one molar solutions might be appreciably different. Of the two, molal solutions are less frequently employed.

A third kind of standard solution is the *normal* solution. This type is discussed in connection with the study of reactions between acids and bases (Sec. 12.11).

10.5. Solubility

Returning for the moment to the discussion of saturation and to Fig. 59, it should be recalled that the extent to which sugar may be dissolved by a fixed quantity of water is limited. The quantity of solute that can be dissolved in a given quantity of solvent is called the *solubility* of that solute. Although any convenient units may be used, solubilities are usually expressed in grams of solute per 100 g. (or 100 ml.) of solvent. The solubilities of a few solids in water are listed in Table 13 together with the descriptive terms usually employed in referring to substances having solubilities of the indicated order of magnitude.

Not all solutes are of limited solubility. The solubility of gases in gases is without limit, since the composition of a gaseous mixture may be adjusted to any desired composition. In some cases, the solubility of liquids in liquids is limited, while in other liquid-liquid mixtures no such limitation exists and the two liquids are said to be *miscible* in all proportions.

TABLE 13

SOLUBILITY OF SOME SOLIDS IN WATER AT 18°C.

Solute	Solubility, g. solute per 100 ml. water	Qualitative description
Sodium chlorate ($NaClO_3$)	97.16	Very soluble
Magnesium nitrate [$Mg(NO_3)_2$]	74.31	
Sodium chloride (NaCl)	35.86	Moderately soluble
Potassium nitrate (KNO_3)	30.34	
Barium hydroxide [$Ba(OH)_2$]	3.7	Sparingly or slightly soluble
Lead chloride ($PbCl_2$)	1.49	
Calcium sulfate ($CaSO_4$)	0.2	
Zinc fluoride (ZnF_2)	0.005	Insoluble*
Silver chloride (AgCl)	0.00013	
Barium sulfate ($BaSO_4$)	0.00023	

* No substance is absolutely insoluble, but for all practical purposes substances of extremely low solubility may be so considered.

10.6. Factors That Influence Solubility

The solubility of a pure solute in a pure solvent is definite only under specified experimental conditions. The solubility of solids in liquids

is markedly dependent upon temperature, while the solubility of gases in liquids is influenced by both temperature and pressure. Two additional factors that may have a bearing on the solubility of a given solute are (1) the presence of other solutes and (2) the occurrence of a chemical reaction between the solute and the solvent.

As a general rule, each solute dissolves in and saturates the solution without being greatly affected by the presence of other solutes, but this is not always true. An exception to the general rule is found in the influence of the presence of hydrogen chloride upon the solubility of sodium chloride in water. If the solubility of NaCl in water is measured accurately, it is found to be, for example, 35.86 g. of NaCl per 100 ml. of water at 18°C. If now the solubility of NaCl in water saturated with hydrogen chloride gas is determined, the solubility is found to be much less than the above value. To prove the same point by another approach, if HCl gas is bubbled into a saturated solution of NaCl in water, crystals of NaCl separate from the solution. In still other instances, the solubility of one solute is enhanced by the presence of one or more other solutes.

Chemical interaction of solute and solvent (or of one solute and another) also is encountered frequently. Thus, salts that combine with molecules of the solvent (Sec. 11.6) are usually more soluble than those salts which dissolve without chemical combination with the solvent. The extensive solubility of ammonia in water is to some extent due to the combination of molecules of ammonia with molecules of the solvent to form the base known as *ammonium hydroxide.*

$$NH_3 + HOH \rightarrow NH_4OH$$

Bromine is only slightly soluble in water but is extensively soluble in water containing dissolved sodium bromide (NaBr), and this enhanced solubility is believed to result from reaction between the bromine and sodium bromide. It is extremely difficult, if not impossible, to draw a sharp line of demarcation between those processes of solution which do and those which do not involve chemical changes of some sort. Unless otherwise specified, the following discussion (as well as that of Chap. 11) assumes that chemical reaction between solvent and solute either is absent or is without bearing upon the topics under consideration.

Influence of Temperature and Pressure upon the Solubility of Gases in Liquids. When a glass container filled with ice water (at 0°C.) is allowed to stand and warm to room temperature, small bubbles of gas are seen to collect around the walls of the container and finally to rise to the surface and escape from the solution. This simple experi-

ment proves that the solubility of the gas (in this case the air that was already dissolved in the water) is less at room temperature than it is at 0°C. In general, the solubility of gases in liquids *decreases* with an increase in temperature.

At any given temperature, the solubility of gases *increases* with increase in pressure and is directly proportional to the applied pressure. This is a statement of *Henry's law*. If a gas is confined over water in a cylinder fitted with a movable piston (Fig. 60) and the piston is at such position (A) that the pressure upon the gas is 1 atm., a certain definite quantity of the gas is dissolved by the available solvent. If now the piston is moved so that the gas is placed under a pressure of 2 atm. (position B), the solubility of the gas is doubled. If a mixture of gases is used, each gas dissolves to an extent that is dependent only upon its partial pressure in the mixture and not upon the presence of the other gases in the mixture.

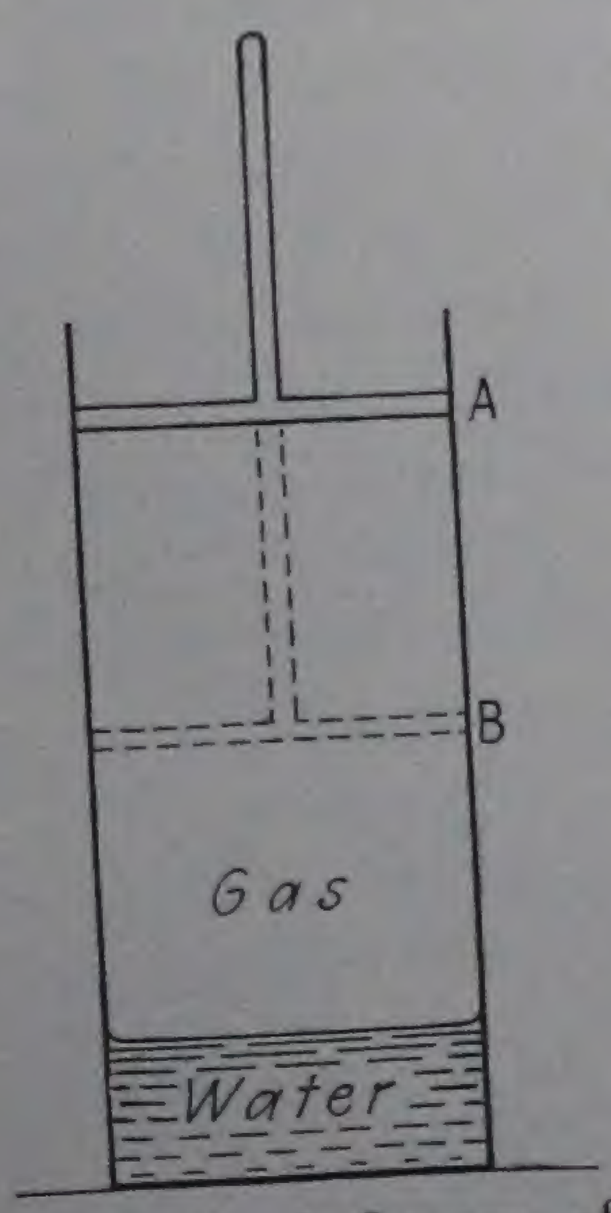

FIG. 60. Influence of pressure upon the solubility of a gas in a liquid.

The sequence of events that accompany the opening of a cold bottle of soda water serves to illustrate the effects of both pressure and temperature. When the cap is first removed, the sudden evolution of carbon dioxide gas provides evidence that this gas is less soluble at atmospheric pressure than at the pressure existing within the unopened bottle. The effect of temperature is shown by the progressive liberation of carbon dioxide as the contents of the bottle slowly warm to the temperature of the surrounding atmosphere.

Influence of Temperature upon the Solubility of Solids in Liquids. In general, the solubility of solids in liquids *increases* with increase in temperature. However, a few solids such as calcium sulfate ($CaSO_4$), calcium chromate ($CaCrO_4$), cerous sulfate [$Ce_2(SO_4)_3$], and calcium hydroxide [$Ca(OH)_2$] behave in just the opposite manner. The solubility of a number of solids in water and their variation in solubility over the temperature range of 0° to 100°C. are shown graphically in Fig. 61. If a solution is saturated at 25° and the temperature is then increased to 30°, more solute dissolves until a new equilibrium is established (*i.e.*, the solution again becomes saturated at the higher temperature. If the solution is then cooled to the original temperature of 25°, crystals of the solute separate from the solution in

an amount equal to that which dissolved because of the increase in temperature. This behavior is observed in all cases except those in which supersaturation occurs. Occasionally crystals do not separate immediately when a saturated solution is cooled. At the lower tem-

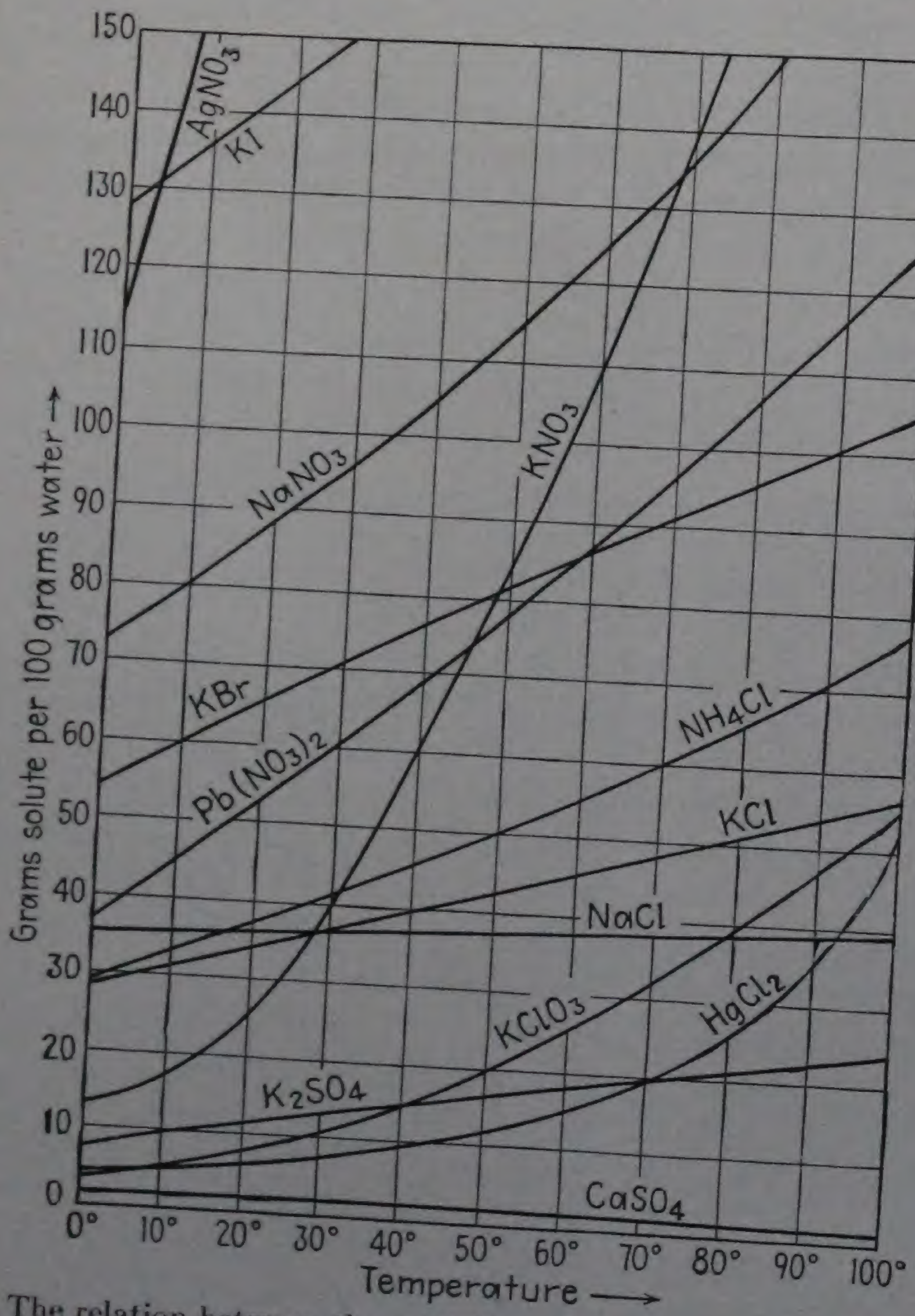

FIG. 61. The relation between the solubility of certain salts and temperature.

perature, then, such a solution contains more dissolved solute than is normally present at that temperature and is therefore described as a *supersaturated* solution. Crystals usually may be obtained readily from a supersaturated solution by stirring the solution vigorously or by inoculating or "seeding" the solution with a crystal of the same composition as the solute. Even tiny dust particles, which serve as

centers about which crystal growth may occur, are sufficient to induce crystallization from a supersaturated solution.

Rates of Solution. Particularly in connection with solutions of solids in liquids, care should be exercised in order to avoid confusion between the *extent of solubility* and the *rate of solution*. At any given temperature, a particular sample of a solid may be very soluble and yet appear to dissolve only slowly. The rate at which a solid dissolves in a liquid depends upon the extent of contact between the solvent and the surface of the solid. Thus, a single crystal of salt weighing 1 g. dissolves in water much more slowly than does 1 g. of the finely powdered salt in the same quantity of water at the same temperature. If one wishes to increase the rate at which a solid dissolves in a liquid, increased surface contact between solid and solvent may be had by the use of a finely divided solid and by agitating (stirring) the mixture.

10.7. Recrystallization as a Means of Purifying a Solid

When a solution containing two solutes is cooled, crystals of the less soluble solute begin to separate from the solution as soon as the saturation point of this solute is reached. The crystals that appear are of the particular crystal type characteristic of the given solid substance and usually do not contain molecules of the more soluble solute. Apparently, the molecules of the second substance usually do not fit into the particular crystal pattern that is being built. Should the solution be cooled sufficiently or should the two solutes be of comparable solubility, each usually crystallizes independently and in its own characteristic crystalline form.

Advantage is taken of this behavior in the purification of solids. Suppose, for example, that it is desired to obtain pure potassium chlorate from an impure sample consisting of 40 g. of $KClO_3$ contaminated with 10 g. of KCl. If this solid mixture is dissolved in 100 ml. of water at 100°C., then cooled, crystals of $KClO_3$ begin to separate from the solution when the temperature reaches about 80° (see Fig. 61) and continue to separate as the temperature is lowered further. Even if cooled to a temperature near 0°C., the KCl remains in solution since the solubility of KCl is about 28 g. per 100 ml. of water at 0°. The crystals of $KClO_3$ may be separated from the solution by filtration.

The foregoing illustration gives a somewhat idealized picture of the process of purification by recrystallization. In actual practice, the first "crop" of crystals obtained is seldom of a high degree of purity, and succeeding crops (which may be filtered off periodically as the temperature is lowered through certain intervals) are still more greatly

contaminated by small quantities of the impurities. This is particularly true if the solubility of the impurities is not greatly different from that of the desired pure substance. However, if the first crops of partly purified material are again recrystallized from water, a product of the desired degree of purity may be obtained. A solid that has been purified in this manner is said to have been *recrystallized*, and if the crops of crystals that separate from the solution as the temperature is lowered through definite intervals are collected separately, the process is referred to as one involving *fractional crystallization*.

10.8. Common Solvents

From the preceding discussions it is evident that one may choose from an almost unlimited variety of solvents including solids, liquids, and gases. In spite of this fact, however, the great bulk of presently available knowledge of solutions centers about a single solvent, *viz.*, water. The fact that chemical developments of the past have emphasized the chemistry of solutions in water suggests that real opportunities for future developments lie in the study of solvents other than water. To the extent that it serves as a solvent for inorganic substances, water occupies a unique position; it is, on the other hand, a relatively poor solvent for organic substances. Solutions in which water is the solvent are commonly referred to as *aqueous* solutions. Other solutions (or substances in general) that contain no water are said to be *anhydrous*.

In recent years, two additional inorganic solvents have come to be used more commonly in chemical work. These are ammonia and sulfur dioxide, both of which are gases under ordinary atmospheric conditions but which may be employed as liquid solvents at low temperatures and/or under pressure. In addition to being fairly good solvents for inorganic solutes, ammonia and sulfur dioxide are also excellent solvents for organic substances.

Some of the more important organic solvents are acetone, alcohols such as methyl and ethyl alcohols, diethyl ether, and benzene. The chemical nature of these materials is considered in some detail in Chaps. 31 to 34. In general, these organic liquids serve well as solvents for organic solutes but exhibit only very limited capacities to dissolve inorganic substances.

GENERAL EXERCISES

1. Define the following terms: (*a*) solution, (*b*) solvent, (*c*) solute, (*d*) molar solution, (*e*) molal solution, (*f*) saturated solution.

2. Distinguish clearly between the following terms: (*a*) dilute and concentrated solutions, (*b*) standard solution and molar solution, (*c*) molar and molal solutions, (*d*) true solution, colloid, and suspension, (*e*) compound and solution.

3. What is meant when the following expressions are used: (*a*) an insoluble substance, (*b*) miscible liquids, (*c*) soluble in water, (*d*) a supersaturated solution, (*e*) the solubility of a substance?

4. How is the solubility of a gas in a liquid influenced (*a*) by an increase in pressure, (*b*) by a decrease in temperature?

5. What generalization may be made with regard to the influence of temperature upon the solubility of solids in liquids?

6. What difficulty would be encountered if one attempted to prepare a 1 *M* solution of silver chloride?

PROBLEMS

1. Determine the weight of solute required to prepare each of the following solutions:

(*a*) 1 liter of 0.5 *M* alcohol (C_2H_6O) solution
(*b*) 3 liters of 1 *M* sodium chloride solution
(*c*) ½ liter of 0.3 *M* glycerol ($C_3H_8O_3$) solution
(*d*) 100 ml. of 0.1 *M* hydrogen chloride solution
(*e*) 1 ml. of 0.01 *M* sodium bromide solution
(*f*) 4 liters of 0.25 *M* ammonium sulfate solution
(*g*) 50 ml. of 0.005 *M* aluminum nitrate solution
(*h*) 1 liter of 1.4×10^{-5} *M* barium iodide solution

2. Calculate the molarity of solutions containing

(*a*) 1.6 g. of $K_2Cr_2O_7$ in 200 ml. of solution
(*b*) 199.2 g. of KI in 1 liter of solution
(*c*) 165 g. of $(NH_4)_2SO_4$ in 200 ml. of solution
(*d*) 0.125 g. of $CuSO_4 \cdot 5H_2O$ in 100 ml. of solution

3. If one should dissolve exactly 10 g. of sodium chloride in sufficient water to make 15 liters of solution, what would be the molarity of this solution?

4. A solution is prepared by dissolving 350 g. of ethylene glycol ($C_2H_6O_2$) in enough water to make exactly 2 liters of solution. Express the concentration of this solution in terms of (*a*) molarity, (*b*) grams of solute per milliliter of solution, and (*c*) molecules of solute per liter of solution.

5. If a solution of alcohol is 1.54 molal, how many grams of alcohol are dissolved in 250 g. of water in this solution?

6. Calculate the molality of glucose ($C_6H_{12}O_6$) solutions containing

(*a*) 90 g. of glucose in 1000 g. of water
(*b*) 180 g. of glucose in 200 g. of water
(*c*) 0.65 mole of glucose in 250 g. of water

7. What weight of calcium chloride must be dissolved in 300 g. of water to make a solution that is 1.23 molal?

SUGGESTED READING

Journal of Chemical Education

Dunning, Pratt, and Lowman, What Starts Precipitation from a Supersaturated Solution? **11,** 624 (1934).

Rohrman and Taylor, The Preparation of Large Crystals of Chrome Alum and Interpretation of Some Etch Figures, **6,** 473 (1929).

Bateman and Fernelius, Demonstration of a Negative Temperature Coefficient of Solubility, **14,** 315 (1937).

Bacon, Use of Calcium Acetate in the Demonstration of a Substance Showing a Negative Coefficient of Solubility, **15,** 494 (1938).

Kobe, Demonstration of an Inverted Solubility Curve, **16,** 183 (1939).

Fernelius and Johnson, Liquid Ammonia as a Solvent, **5,** 664 (1928).

CHAPTER 11

PHYSICAL PROPERTIES OF SOLUTIONS

From the study of the properties of liquids (Chap. 7), it should be recalled that each pure liquid is characterized by definite physical properties such as boiling temperature, freezing temperature, and vapor pressure. The following discussion is concerned with the manner in which these physical properties are altered by the presence of solutes. With one exception, only nonvolatile solutes are considered in this discussion. If the influence of a solute is to be studied, it is certainly desirable that it remain in the solution so that its effects may be studied over a period of time. Volatile solutes would also complicate the study of the vapor pressures of solvents since the solute molecules themselves would escape and exert measurable vapor pressures. Acids, bases. and salts are excluded for other reasons which become apparent later.

11.1. Lowering of the Vapor Pressure

When a nonvolatile solute is dissolved in a pure solvent, the vapor pressure of the resulting solution is less than the vapor pressure of the pure solvent at the same temperature. The extent to which the vapor pressure of the solvent is lowered is directly proportional to the ratio of the *number* of solute molecules to the total number of molecules in the solution. Thus, 1 gram-molecular weight of naphthalene ($C_{10}H_8$) (128 g. containing 6.02×10^{23} molecules) dissolved in acetone lowers the vapor pressure of acetone just exactly as much as does 1 gram-molecular weight of camphor ($C_{10}H_{16}O$) (152 g. also containing 6.02×10^{23} molecules), dissolved in an equal quantity of acetone. Consequently, it would seem that the lowering of the vapor pressure depends only upon the number and not upon the kind of solute molecules present. The correctness of this assumption becomes apparent when one attempts, in terms of the kinetic-molecular theory, to visualize the manner in which the presence of solute molecules operates to decrease the vapor pressure of the solvent.

The escape of solvent molecules from the liquid occurs at the surface of the liquid. In Fig. 62*a*, molecules in the surface of a pure liquid solvent are represented as being in equilibrium with solvent molecules in the vapor state, and therefore exerting the normal solvent vapor

pressure at the given temperature. In the solution (Fig. 62*b*), the exposed surface is partly occupied by molecules of the nonvolatile solute, and the available surface from which the escape of solvent molecules can occur is correspondingly diminished. Furthermore, in the body of the liquid, those solvent molecules which have higher than average kinetic energies and which would tend to move to the surface and escape are impeded by the presence of solute molecules. As a result, fewer solvent molecules can escape from the liquid to exert pressure upon the surface of the liquid. At the same temperature, an increase in the number of solute molecules would serve further to lower the vapor pressure.

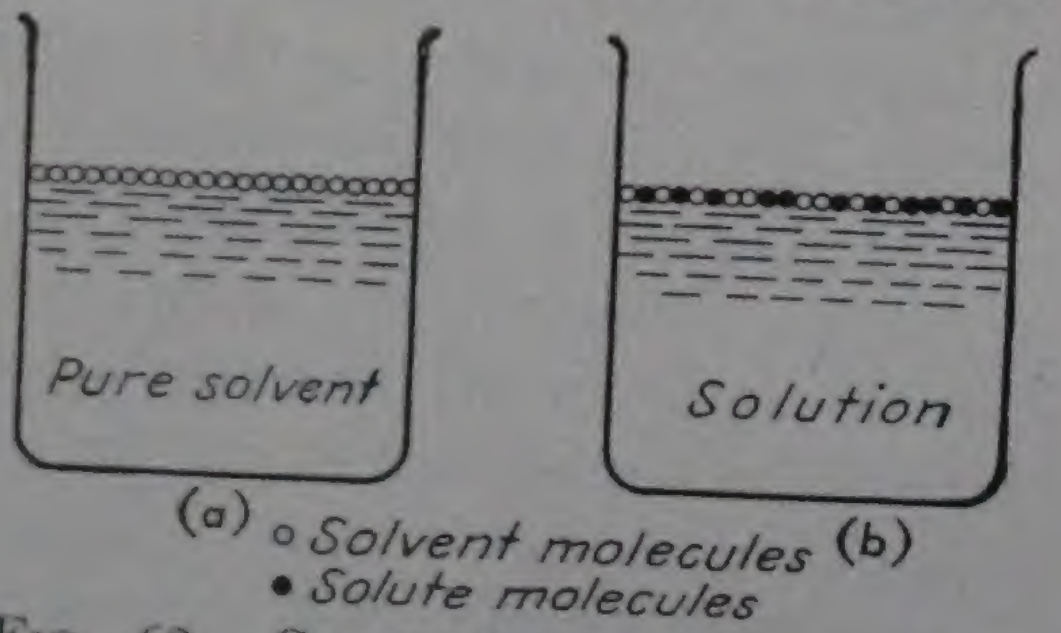

FIG. 62. Comparison of the surface layer of molecules in a pure solvent and a solution.

Deliquescence. A practical example of the lowering of vapor pressure is found in the behavior of substances that exhibit the property of deliquescence. Some solids that are very soluble in water form solutions on their surfaces when exposed to an atmosphere containing sufficient water vapor. When solid zinc chloride ($ZnCl_2$) or potassium hydroxide (KOH), for example, is exposed to the air, its surface quickly becomes covered by a thin film of solution. This behavior is known as *deliquescence*, and the solid substance is said to be *deliquescent* or *hygroscopic*. Because of the presence of dissolved KOH, the vapor pressure of this solution is less than the partial pressure of the water vapor in the surrounding atmosphere. Consequently, the water vapor enters the solution from the air, and the solid is all dissolved. Furthermore, water vapor from the atmosphere continues to enter and dilute the solution until the vapor pressure of the solution becomes the same as (reaches equilibrium with) the partial pressure of water vapor in the atmosphere.

Use is made of this phenomenon in keeping down the dust on unsurfaced roads. Calcium chloride ($CaCl_2$) is a cheap commercial product which is extremely deliquescent. When sprinkled upon the surface of a dusty highway, the $CaCl_2$ attracts moisture from the atmosphere and forms a solution which moistens the road surface and prevents the rise of dust particles. This application is, of course, entirely useless in hot, arid climates where the partial pressure of water vapor in the atmosphere is less than the vapor pressure of a saturated solution of calcium chloride.

11.2. Elevation of the Boiling Temperature

The boiling of a pure liquid has been pictured as the condition that obtains when the kinetic energy of the molecules of the liquid has been increased (by application of heat energy) to such extent that the vapor pressure of the liquid exceeds the opposing atmospheric pressure. At an atmospheric pressure of 760 mm., the boiling temperature of pure water is 100°C. If the temperature of water containing a nonvolatile solute is raised to 100°C., boiling does not occur; the kinetic energy of the water molecules is not large enough to overcome both the opposing atmospheric pressure and the interference offered by the solute molecules. This is simply another way of saying that the vapor pressure of the solution at 100°C. is less than the opposing atmospheric pressure, for it has already been shown that the vapor pressure of a solution is less than that of the pure solvent at the same temperature. The result is that the temperature must be raised above 100° in order to cause the solution to boil.

Just how much elevation in temperature is required to produce boiling depends upon exactly the same factor that determines the extent of lowering the vapor pressure, *viz.*, the *relative number* of solute molecules present. At 760 mm., a solution consisting of 1 mole of sugar (342 g.) dissolved in 1000 g. of water boils at 100.515°C., which is exactly the same as the boiling temperature of a solution consisting of 1 mole of glycerol (92 g.) dissolved in 1000 g. of water. Both solutions boil at the same temperature despite the great difference in total weight of solute because both solutions contain exactly the same number of solute molecules. Excluding acids, bases, and salts, a 1 molal aqueous solution boils 0.515° above the normal boiling temperature of pure water. With solvents other than water, the extent of elevation in boiling temperature is different from 0.515° but is nevertheless definite for each solvent.

Fractional Distillation. When a mixture of two liquids having different vapor pressures (and therefore different boiling temperatures) is heated, boiling occurs when the combined vapor pressures of the two liquids exceeds the opposing atmospheric pressure. The results obtained by continued boiling of such a mixture may be understood best in terms of a specific example. If a mixture consisting of equal volumes of alcohol (which boils at 78.4° at 1 atm.) and benzene (which boils at 80.4° at 1 atm.) is placed in the boiler of a distillation apparatus (Fig. 63) and heated to boiling, the vapors that leave the liquid may be condensed upon coming into contact with the cold inner surface of the condenser and collected in a suitable container. The first liquid

(distillate) to be collected is a mixture consisting largely of alcohol but containing some benzene. As the distillation continues, the temperature rises and the vapors that leave the liquid become increasingly richer in benzene (the higher boiling component of the mixture) and contain less and less alcohol. This must occur if boiling is to continue. Initially, the alcohol exerts the major fraction of the total vapor pressure of the mixture. As the alcohol is distilled from the mixture, the temperature must increase enough to raise the partial pressure of

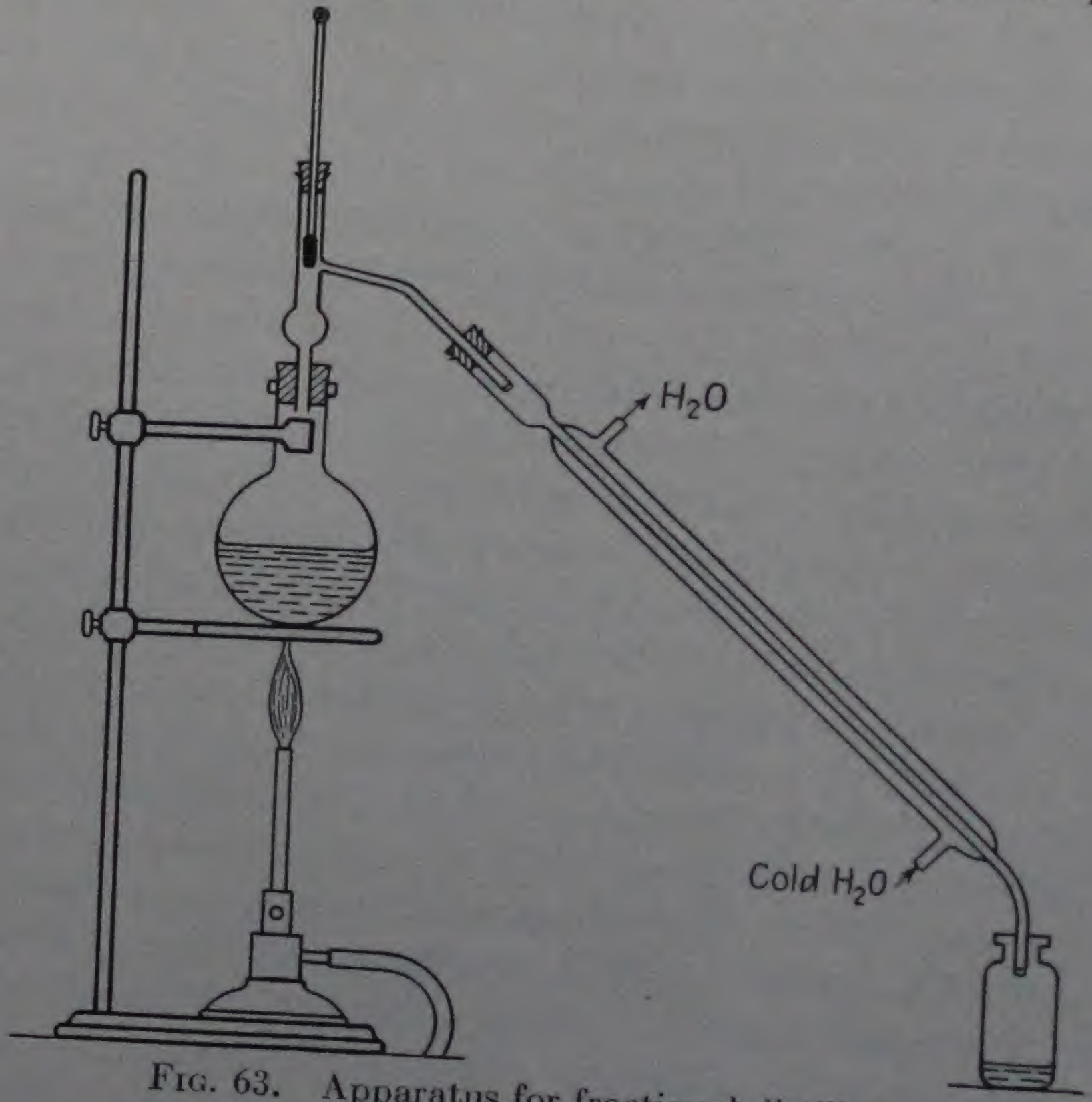

FIG. 63. Apparatus for fractional distillation.

benzene sufficiently to overcome the loss in total vapor pressure occasioned by the removal of alcohol. Finally, the last vapors to leave the liquid are relatively richer in benzene and contain but little alcohol. If the vapors are condensed and collected in, for example, three portions or fractions, the first is largely alcohol, the last collected is largely benzene, and the middle fraction is a more nearly equal mixture of the two. If the first and third fractions are separately subjected to one or more additional distillations of the same sort, pure alcohol and pure benzene may be secured.

This process is known as *fractional distillation*. It is employed extensively in the separation of crude petroleum into fractions such as

gasoline, kerosene, and lubricating oil. Many other liquid industrial products are separated and purified by similar operations.

11.3. Lowering of the Freezing Temperature

At the freezing temperature of a pure solvent, solid exists in equilibrium with liquid, and the vapor pressure of the solid is identical with that of the liquid. For water at a pressure of 1 atm., this condition is realized at 0°C. When the temperature of a dilute aqueous solution of a nonvolatile solute is lowered to the freezing temperature, only crystals of the solvent appear, and this is found to occur at a temperature *below* the freezing temperature of the pure solvent. At this lower temperature, the vapor pressure of the solvent crystals is equal to the solvent vapor pressure of the solution, a condition which can be realized only at a temperature lower than the normal freezing temperature of the pure solvent.

Again, the situation is amenable to explanation on the basis of the kinetic-molecular theory. Homogeneous distribution of solute molecules throughout the body of the liquid increases the average distance between solvent molecules. The force of attraction between molecules, which tends to arrange the molecules of the solvent into the definite geometric pattern of the crystal, cannot be so effective over this greater average distance. In order for the forces of attraction to operate, it is necessary that the kinetic energy of the solvent molecules be lessened, since it is the kinetic energy that acts in opposition to the forces of attraction or cohesion. The kinetic energy is decreased by lowering the temperature below the normal freezing temperature of the pure solvent. The extent to which the temperature must be lowered is obviously dependent upon the *relative number* of solute molecules present in the particular solution.

Again excluding acids, bases, and salts, 1 mole of sugar (342 g.), 1 mole of glycerol (92 g.), or 1 mole of any other nonvolatile solute dissolved in 1000 g. of water (*i.e.*, 1 *m* solutions) forms a solution having a freezing temperature of −1.86°C., since all these 1 molal solutions contain the same number of solute molecules. With other solvents, the extent of lowering of the freezing temperature is different, but definite.

A familiar application of this lowering of the freezing temperature of liquids is found in the use of antifreeze mixture in automobile radiators. Alcohol, glycerol, ethylene glycol, etc., mixed with water produce solutions having freezing temperatures lower than that of pure water.

Freezing Mixtures. Advantage of lowering in freezing temperature is also taken in the production of low temperatures required for a

variety of purposes. Salt added to ice at 0°C. dissolves in the thin layer of liquid surrounding each piece of solid ice. The resulting solution has a vapor pressure less than that of the ice; hence, some ice melts. Of course this melting is accompanied by an absorption of heat, and if the ice is so insulated that it cannot absorb heat from its surroundings, the heat is absorbed from the ice itself. Accordingly, the temperature of the mixture falls. Ice and sodium chloride produce a temperature of −22°C., while ice and the more soluble calcium chloride provide temperatures as low as −56°C.

11.4. Osmosis

Another important behavior exhibited by solutions is the phenomenon of *osmosis*. Certain membranes, notably the lining of eggshells, fish bladder, parchment paper, or even purely inorganic jellies such as copper ferrocyanide or copper silicate, are of such character that certain kinds of molecules are capable of passing through these membranes, while other kinds of molecules cannot. A membrane that is permeable by one kind of molecule and not by another is called a *semipermeable* membrane. Frequently, it is found that such membranes are permeable by solvent but not permeable by solute molecules. When a solution of sugar in water is enclosed in a bag made of one of these membranes, or enclosed in a porous earthenware cup the pores of which are filled with an inorganic jelly such as copper ferrocyanide (Fig. 64), and the bag or cup is immersed in a less concentrated solution of sugar or in pure water, it is observed that water passes into the bag or cup. This indicates that there is a net transfer of water molecules from the more dilute sugar solution or from the pure water into the more concentrated solution enclosed by the semipermeable membrane. This means that water molecules move from the region where the concentration of water molecules is greater (the dilute sugar solution or pure water) to the region containing a lower concentration of water molecules (the concentrated sugar solution). Water molecules also move in the opposite direction but at a lesser rate. **The passage of solvent through a semipermeable membrane from a region of greater**

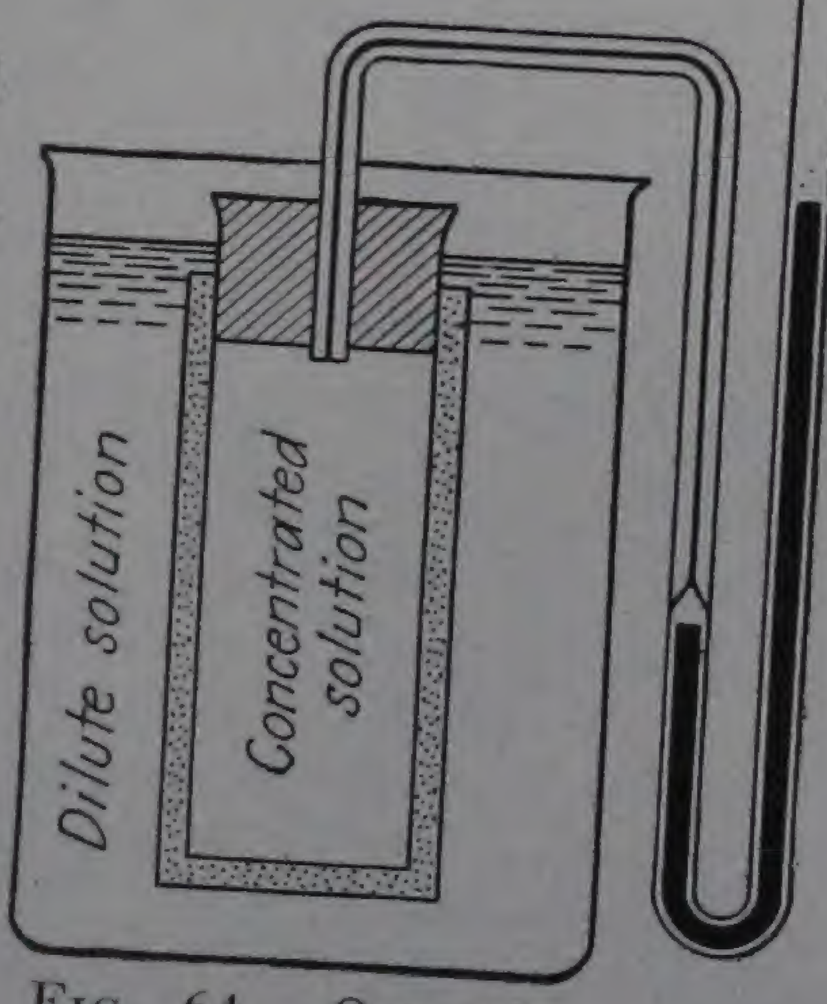

FIG. 64. Osmotic-pressure cell.

solvent concentration into a region of lower solvent concentration is called osmosis.

The semipermeable membrane is free from holes, but it allows water and not sugar molecules to pass through it.

Osmotic Pressure. In an experiment utilizing an apparatus of the type shown in Fig. 64, water passes from the beaker into the cell. This results in an increase in the volume of the sugar solution contained within the cell. By submitting the solution in the cell to an increase in pressure, this net transfer of solvent molecules may be prevented. The pressure that is just sufficient to prevent a net transfer of solvent molecules into the solution is termed the *osmotic pressure* of the solution. The magnitude of this pressure is proportional to (*a*) the concentration of solute molecules and (*b*) the absolute temperature. For a 1 molal solution of sugar relative to pure water, the osmotic pressure at 0° amounts to approximately 22.4 atm., and since the osmotic pressure is proportional to the absolute temperature, the osmotic pressure at 25°C. is approximately

$$22.4 \times {}^{298}\!/_{273} = 24.5 \text{ atm.}$$

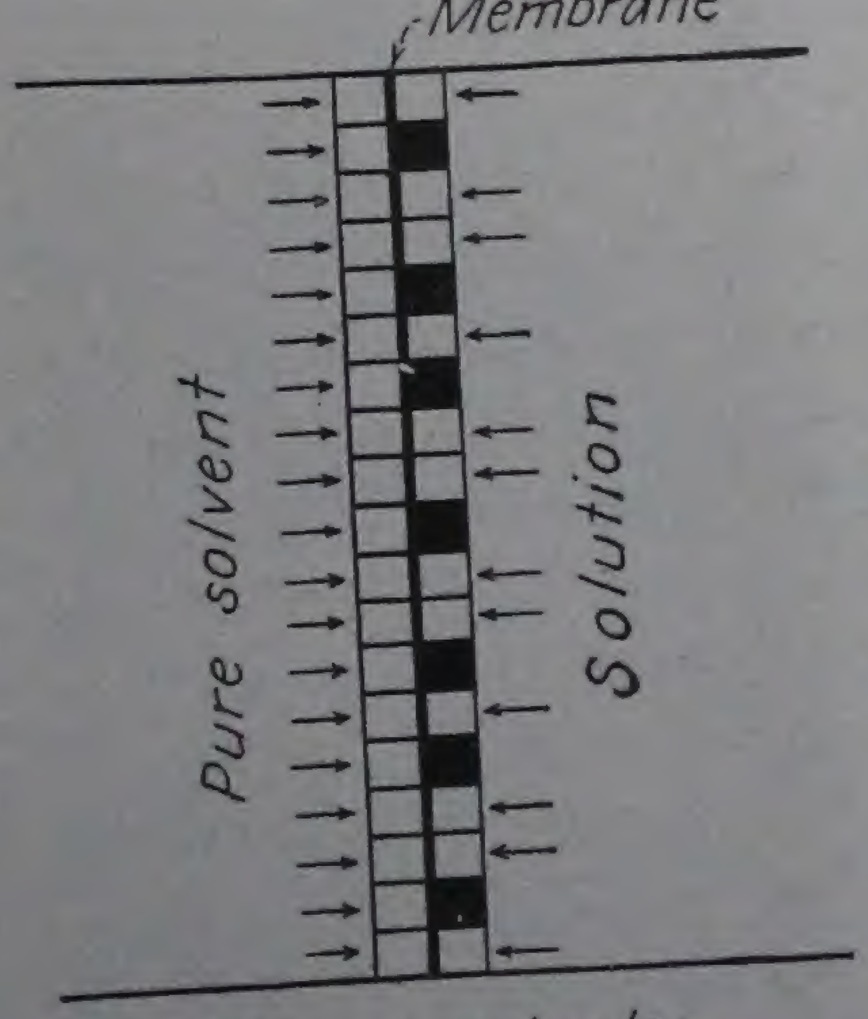

FIG. 65. Diagram illustrating the relative number of impacts by solvent molecules on either side of a semipermeable membrane.

The mechanism by which osmosis occurs may be explained in much the same manner as the lowering of the vapor pressure. The rate of absorption of water by the membrane is proportional to the number of impacts by water molecules per unit of area per unit of time. Initially, the number of impacts is greater on the side exposed to pure water than on the side exposed to the sugar solution. This is true because (1) the concentration of water molecules is greater on that side, and (2) on the side exposed to the solution, a part of the surface of the membrane is covered by sugar molecules (Fig. 65). Consequently, the rate of absorption of water is greater on the side exposed to pure water, and there is a resultant net transfer of solvent into the solution. More water molecules move into the solution in unit time than move out of the solution. When, however, the solution is put under pressure (or pressure is built up hydrostatically owing to the increase in the volume

of the solution), the concentration of water molecules is increased in the solution; the unoccupied space between molecules is lessened by compression. If the applied pressure is sufficient, the rate of absorption of water molecules on the side of the membrane exposed to the solution may be made equal to the rate of absorption on the side exposed to pure water. The rates of transfer of water molecules in the two directions are equal, a condition of dynamic equilibrium exists, and there is no net transfer of solvent molecules.

Applications of Osmosis. Solutions that exhibit the same osmotic pressure would exist in equilibrium when placed on opposite sides of a semipermeable membrane. The term *isotonic* is usually applied to solutions that have the same osmotic pressure. When solutions are injected into the blood stream either for purposes of medication or to replace blood that has been lost, the solution injected and the blood must be isotonic. Pure water injected into the blood stream in any appreciable quantity may prove fatal since water molecules will pass out of the blood stream and into the surrounding tissues and even into the corpuscles. Osmosis is of tremendous importance in biology, medicine, and other related sciences. The germination of seeds, the rise of sap into the branches and leaves of trees, and the nutrition of both plants and animals are only a few of the many common occurrences that involve the phenomenon of osmosis.

Some membranes are permeable not only to solvent molecules but also to certain kinds (but not all kinds) of solute molecules. It is through this selective action of membranes that the fluid in the stomach is acidified. A similar behavior is involved in the extraction of sugar from sugar beets. If the sliced beets are placed in a vessel through which a steady flow of pure water is maintained, the sugar passes through the cell walls of the beet and into the surrounding water while the other constituents of the beet are, in the main, not capable of permeating the cell wall. The explanation of this phenomenon may lie in the difference in size of the solute particles; the membrane may be permeable to particles of molecular size and not to particles of colloidal size.

11.5. Determination of Molecular Weights of Liquids and Solids

It was indicated in Sec. 8.8 that a knowledge of the properties of solutions provides a basis for the experimental measurement of the relative weights of molecules of liquids and solids. The two properties most commonly utilized in this connection are the lowering of the

freezing temperature and the elevation of the boiling temperature. It has been emphasized repeatedly that the properties of solutions are dependent upon the number of solute molecules present. If 1 mole of sugar containing 6.02×10^{23} molecules could be dissolved in 1000 g. of benzene, it would lower the freezing temperature 5.12° and raise the boiling temperature 2.57°. Accordingly, if one measures the extent to which the boiling temperature or freezing temperature of a given weight of benzene is changed by the presence of a known weight of solute, the molecular weight of the solute may be calculated by comparison with the known behavior of sugar. Before specific examples are considered, it should be pointed out that the substances used here for purposes of illustration are chosen at random and that many other solutes and solvents could be employed equally well. Further, it should be indicated that this application requires that the solute dissolve in the solvent without the occurrence of any chemical change that would affect the relative weights of the solute molecules.

Fifty grams of pure benzene was found to freeze at 5.50°C. The addition of 1.5 g. of a pure solute lowered the freezing temperature to 3.86°C. The presence of 1.5 g. of solute therefore resulted in a lowering amounting to $5.50 - 3.86 = 1.64°$. The molecular weight of this solute is that weight which would lower the freezing temperature of 1000 g. of benzene 5.12° and may be calculated as follows:

Wt. of solute in 50 g. benzene = 1.5 g.

Wt. of solute in 1000 g. of benzene $= 1.5 \times {}^{1000}\!/_{50} = 30$ g.

Freezing-temperature lowering produced by 30 g. solute in 1000 g. benzene $= 5.50 - 3.86 = 1.64°$

Freezing-temperature lowering produced by 1 gram-molecular weight of solute in 1000 g. benzene = 5.12°

Hence, by simple proportion,

Mol. wt. of solute : 5.12 : : 30 : 1.64

$$\text{Mol. wt. of solute} = 30 \times \frac{5.12}{1.64} = 93.6$$

With the boiling-temperature-elevation method, the 50 g. of pure benzene was found to boil at 80.20°C., and the addition of 1.5 g. of solute produced a solution that boiled at 81.02°, or an elevation amounting to 0.82°C. Given the additional information that the presence of 1 gram-molecular weight of the solute in 1000 g. of benzene

would result in a boiling-temperature elevation amounting to 2.57°, one may calculate the molecular weight of the solute.

Wt. of solute in 50 g. benzene = 1.5 g.

Wt. of solute in 1000 g. benzene = $1.5 \times {}^{1000}/_{50} = 30$ g.

Boiling-temperature elevation produced by 30 g. solute in 1000 g. benzene = 81.02 − 80.20 = 0.82°

Boiling-temperature elevation produced by 1 gram-molecular weight of solute in 1000 g. benzene = 2.57°

Hence,

Mol. wt. of solute : 2.57 : : 30 : 0.82

$$\text{Mol. wt. of solute} = \frac{2.57 \times 30}{0.82} = 94.0$$

This value, allowing for experimental errors in either set of data, agrees very well with the value of 93.6 obtained by the method involving the lowering of the freezing temperature.

11.6. Solvation

The regularities observed in the influence of many solutes upon the physical properties of pure solvents are not realized if the solute undergoes chemical change upon being dissolved in a pure solvent. The kinds of chemical change that may occur are of several different types. The solute molecule may *dissociate* to form smaller units of matter, or it may *associate* either with other solute molecules or with solvent molecules to form larger units.

If solute molecules (or atoms, or ions) become associated with molecules of the solvent, they are said to be *solvated* and this variety of chemical reaction is known as *solvation*. The extent of solvation depends upon the nature of the solute, the nature of the solvent, the temperature, etc. When commercial "soda ash" [sodium carbonate (Na_2CO_3)] is dissolved in water, extensive solvation occurs. Since water is the solvent most generally used, solvation by water is given the special name *hydration*, and the substance formed by the union of, *e.g.*, Na_2CO_3 with water molecules is called a *hydrate*. If a saturated solution of Na_2CO_3 in water is cooled or if the solvent is allowed to evaporate slowly, the crystals that separate from the solution are found to have the composition represented by the formula $Na_2CO_3 \cdot 10H_2O$. This does not prove that the Na_2CO_3 may not have been associated with more than $10H_2O$ *in the solution*. The number of water molecules may have been greater than but probably not less than 10.

Solvent that actually separates in combination with the solute in crystalline form is known as *solvent of crystallization;* in the above case, *water of crystallization.* Thus, a distinction is made between association in solution and association in the crystal. Other examples of salt hydrates are $CuSO_4 \cdot 5H_2O$, $CdCl_2 \cdot 2H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, and $Fe_3(PO_4)_2 \cdot 8H_2O$.

Efflorescence. Many salts containing water of crystallization are somewhat unstable under ordinary atmospheric conditions. Because the crystals contain combined water, the crystal exerts (at any given temperature) a definite water vapor pressure. If the water vapor pressure of the crystal happens to be greater than the partial pressure of water vapor in the atmosphere, the crystal loses water to the surrounding atmosphere. This behavior is known as *efflorescence.* Thus, when $Na_2CO_3 \cdot 10H_2O$ is exposed to dry air, the hydrate loses water of crystallization and is changed to a white powder. When the partial pressure of water vapor in the atmosphere is sufficiently great, dry salts are frequently capable of taking water from the atmosphere (Sec. 11.1).

Salts which contain water of crystallization and which exert a water vapor pressure equal to or greater than that of the surrounding atmosphere may be caused to lose water if the vapor pressure is increased by the application of heat. Sometimes this loss of water by the crystal occurs in a stepwise manner as the temperature is increased. For example,

$$CuSO_4 \cdot 5H_2O + \text{heat} \xrightarrow{110^\circ} CuSO_4 \cdot H_2O + 4H_2O$$

$$CuSO_4 \cdot H_2O + \text{heat} \xrightarrow{230^\circ} CuSO_4 + H_2O$$

GENERAL EXERCISES

1. Define the following terms: (*a*) osmosis, (*b*) osmotic pressure, (*c*) semipermeable membrane, (*d*) isotonic solutions.

2. Distinguish clearly between (*a*) water of hydration and water of crystallization, (*b*) hydration and solvation, (*c*) efflorescence and deliquescence.

3. In ascending a mountain road, the operating temperature of an automobile motor did not increase but the water in the radiator boiled as the automobile approached the summit of a particularly high mountain. Another identical automobile operating at the same motor temperature but containing an antifreeze mixture in the radiator reached the top of the same mountain without boiling the solution in the radiator. (*a*) Why did the water boil in the radiator of the first automobile? (*b*) How can one account for the fact that, under the same conditions, the solution in the radiator of the second automobile did not boil?

4. An antifreeze mixture *A* was prepared by dissolving 1 gal. of ordinary alcohol (C_2H_6O, density = 0.8) in 5 gal. of water. Another mixture *B* was made by dis-

solving 1 gal. of "wood alcohol" (CH_4O, density = 0.8) also in 5 gal. of water. During a cold period, mixture *A* froze and mixture *B* did not. Explain.

5. Of two clear liquids, one is known to be a solution and the other the corresponding pure solvent. Without altering the concentration of the solution in any way, how could one determine which of the two is the solution?

PROBLEMS

The following problems involve calculations based upon lowering of the freezing temperature or elevation of the boiling temperature of pure solvents owing to the presence of solutes. In all of these cases the dissolved substances are assumed to be nonvolatile and to be solutes other than acids, bases, and salts. In all problems involving the calculation of molecular-weight values, the answers should be rounded off to the nearest whole number.

1. A solution consisting of 4.0 g. of a pure solute dissolved in 100.0 g. of pure water was found by experiment to freeze at a temperature of −0.98°C. Calculate the molecular weight of the solute.

2. What would be the boiling temperature of a solution containing 10.0 g. of a solute and 700.0 g. of water, if the molecular weight of the solute is 42?

3. Pure carbon tetrachloride boils at 76.80°C., and a 1 molal solution of a nonvolatile solute in carbon tetrachloride boils at 81.68°C. In a molecular-weight determination, 3.6 g. of a solute dissolved in 88.4 g. of carbon tetrachloride formed a solution which boiled at 80.32°. Calculate the molecular weight of the solute.

4. A solution containing 3.6 g. of a solute in 150.0 g. of water freezes at −0.28°C. What is the molecular weight of the solute?

5. If the molecular weight of a solute is 80, calculate the freezing temperature of a solution containing 25.0 g. of this solute in 400 g. of water.

6. A solution consisting of 3.8 g. of a solute in 250 g. of water boils at 100.09°C. Calculate the molecular weight of the solute.

7. A solution of 4.5 g. of a solute in 40.0 g. of benzene freezes at a temperature 3.5°C. below the freezing temperature of pure benzene. If the molal freezing-temperature-depression constant for benzene is 5.12°, what is the molecular weight of this solute?

8. Approximately what weight of pure alcohol (C_2H_6O) would one have to add to 1 liter of water in order that freezing would not occur if the temperature were lowered to 0°F.?

9. A solution containing 115.0 g. of a solute in 500.0 g. of water freezes at −0.46°C. Calculate the molecular weight of the solute.

10. Forty-two and three-tenths grams of a solute was dissolved in 200.0 g. of water to form a solution which boiled at 100.15°C. What is the molecular weight of the solute?

11. When 15.4 g. of a solute is dissolved in 750.0 g. of ether, the boiling-temperature elevation amounts to 0.086°C. If the molal boiling-temperature-elevation constant for ether is 2.11°C., what is the molecular weight of the solute?

12. What would be the boiling temperature of a solution prepared by dissolving 26.0 g. of sugar ($C_{12}H_{22}O_{11}$) in 100.0 g. of water?

13. A mixture of 5.5 g. of a pure solid and 50.0 g. of pure camphor melts at 154°C. If pure camphor melts at 177° and if the molal freezing-temperature-depression constant for camphor is 40°, what is the molecular weight of the pure solid?

SUGGESTED READING

Journal of Chemical Education

Steinbach, Laboratory Experiments on Deliquescence and Efflorescence, **20**, 146 (1943).

Davidson, A Simple Presentation of the Concepts of Osmosis, Osmotic Pressure, and Osmotic Work, **11**, 499 (1934).

CHAPTER 12

ACIDS, BASES, AND SALTS; NOMENCLATURE

The study and practice of chemistry are greatly simplified if one can think in terms of *types* or kinds of chemical substances and reactions rather than always in terms of specific cases. For example, there are many compounds known as *oxides*, but for most purposes it is not necessary that one become familiar with the detailed behavior of each such compound. Rather, it is desirable to recognize that oxides may be classified according to type and that all oxides of a given type have certain properties in common. Thereafter, a detailed knowledge of the properties of individual oxides may be acquired as needed. The initial problem involved in the study of those classes of compounds known as *acids*, *bases*, and *salts*, therefore, is that of becoming acquainted with the chemical behavior characteristic of these types of compounds. In addition, it is necessary that the student acquire a somewhat more detailed knowledge of a few common representatives of each class.

12.1. Acids

It has already been indicated that acids are compounds containing hydrogen which may be replaced (at least in part) by certain metals. In addition, there are other properties that are exhibited by those acids which are soluble in water. In general, water solutions of acids have a sour taste and have the ability to bring about changes in the colors of certain dyes. When it is brought into the presence of an acid, the blue form of the dye known as *litmus* is changed into a form that exhibits a red coloration. It is well to recognize at the outset that those properties which are thought of as being characteristic of acids are really the properties of water solutions of the compounds called *acids* not so much the properties of the pure compounds themselves.

In the following paragraphs, some common acids are considered under headings that are related to the elemental complexity of the compounds involved. If the molecules of compounds contain two kinds of elements, the compounds are classed as *binary*. Similarly, *ternary* compounds are those consisting of molecules made up of three kinds of elements. (The use of the terms *binary* and *ternary* is by no means restricted to acids.)

Binary Acids. The names of four common compounds, their formulas, and the names applied to their solutions in water (which exhibit acidic properties) are listed in Table 14.

TABLE 14
Common Binary Acids

Compound	Formula	Name of water solution
Hydrogen chloride	HCl	Hydrochloric acid
Hydrogen bromide	HBr	Hydrobromic acid
Hydrogen iodide	HI	Hydriodic acid
Hydrogen sulfide	H_2S	Hydrosulfuric acid

When dissolved in water, these compounds form solutions that exhibit acidic properties. Thus, pure gaseous hydrogen chloride does not exhibit acidic properties, but a water solution of hydrogen chloride is known as *hydrochloric acid*. Binary acids are composed of hydrogen and a nonmetal, but it must be borne in mind that not all such compounds are acids.

Ternary Acids. The ternary acids *may be* formed by the combination of oxides of nonmetals with water. The following equations serve to illustrate the formation of the common ternary acids:

$$\underset{\text{Sulfur trioxide}}{SO_3} + H_2O \rightarrow \underset{\text{Sulfuric acid}}{H_2SO_4}$$

$$\underset{\text{Sulfur dioxide}}{SO_2} + H_2O \rightarrow \underset{\text{Sulfurous acid}}{H_2SO_3}$$

$$\underset{\text{Nitrogen pentoxide}}{N_2O_5} + H_2O \rightarrow \underset{\text{Nitric acid}}{2HNO_3}$$

$$\underset{\text{Phosphorus pentoxide}}{P_2O_5} + 3H_2O \rightarrow \underset{\text{Phosphoric acid}}{2H_3PO_4}$$

$$\underset{\text{Phosphorus trioxide}}{P_2O_3} + 3H_2O \rightarrow \underset{\text{Phosphorous acid}}{2H_3PO_3}$$

$$\underset{\text{Carbon dioxide}}{CO_2} + H_2O \rightarrow \underset{\text{Carbonic acid}}{H_2CO_3}$$

Another common ternary acid is that known as *acelic acid* ($HC_2H_3O_2$). It is not formed in any manner similar to that given for the other common ternary acids and differs from them also in that only one of the four hydrogen atoms can be replaced by metals, a fact that is emphasized by the manner in which the formula is written.

Acid Anhydrides. An inspection of the equations given above suggests a clear-cut relationship between certain nonmetal oxides and certain acids. For example, SO_3 is related to sulfuric acid, and P_2O_3 is related to phosphorous acid in the same sense. **Any nonmetal oxide that reacts with water to form an acid is called an acid anhydride.** Thus, N_2O_5 is the anhydride of nitric acid, SO_2 is the anhydride of sulfurous acid, etc. Literally, the term *anhydride* means "without water."

12.2. Bases

Just as hydrogen is the characteristic component of all acids, so the hydroxyl radical (OH) is the characteristic component of many but not all bases. Bases in water solution have a bitter taste, have a "soapy" feel, and produce an irritant effect upon the skin. Solutions of bases change the colors of certain dyes, and the color changes produced by bases are usually the reverse of the changes produced by acidic solutions. Thus, bases change the color of litmus from red to blue. There are many bases, however, that do not exhibit these properties because of their insolubility in water. In fact, only a few of the common bases are appreciably soluble in water.

Hydroxides are ternary compounds, some of which may be formed directly by the union of oxides of metals with water. Still other bases such as NH_4OH arise by the reaction of other types of compounds with water. The following equations serve to illustrate the formation of a number of common bases which are measurably soluble in water:

$$\underset{\text{Sodium oxide}}{Na_2O} + H_2O \rightarrow \underset{\text{Sodium hydroxide}}{2NaOH}$$

$$\underset{\text{Potassium oxide}}{K_2O} + H_2O \rightarrow \underset{\text{Potassium hydroxide}}{2KOH}$$

$$\underset{\text{Calcium oxide}}{CaO} + H_2O \rightarrow \underset{\text{Calcium hydroxide}}{Ca(OH)_2}$$

$$\underset{\text{Barium oxide}}{BaO} + H_2O \rightarrow \underset{\text{Barium hydroxide}}{Ba(OH)_2}$$

$$\underset{\text{Ammonia}}{NH_3} + H_2O \rightarrow \underset{\text{Ammonium hydroxide}}{NH_4OH}$$

The compound ferric hydroxide [$Fe(OH)_3$] is a typical example of an insoluble base. It might be suggested that $Fe(OH)_3$ might be formed by the union of iron oxide (Fe_2O_3) and water.

$$Fe_2O_3 + 3H_2O \rightarrow 2Fe(OH)_3$$

When Fe_2O_3 is added to water, however, this reaction does not occur to any marked extent because the insoluble particles of Fe_2O_3 quickly become coated with insoluble $Fe(OH)_3$ and this coating effectively protects the remaining Fe_2O_3 from coming into contact with the water required for continuation of the reaction. Obviously then, if one wished to prepare $Fe(OH)_3$, it would be necessary to use some less direct method. As a general rule, only the soluble bases may be formed in appreciable quantity by the reaction of metal oxides and water.

Basic Oxides. By comparison with acid anhydrides, it might appear that the oxides of the metals could be looked upon as base anhydrides. This is seldom done because so few metal oxides actually react with water to form the corresponding bases. The metal oxides are sometimes called *basic oxides*, or simply *bases*. Even though an oxide may not react with water to form the corresponding base, the oxide and the base may be considered as being related in a purely formal way.

12.3. Neutralization

If a given volume of a 1 M solution of hydrochloric acid is mixed with the same volume of a 1 M solution of sodium hydroxide, the resulting solution has neither the properties of an acid nor the properties of a base; it is therefore said to be *neutral*. If this neutral solution is evaporated to dryness, the only solid product remaining is found to be sodium chloride. The equation for the reaction is

$$HCl + NaOH \rightarrow H_2O + NaCl$$

Other acids and bases react similarly, *e.g.*,

$$H_2SO_4 + 2NaOH \rightarrow 2H_2O + Na_2SO_4$$

$$2H_3PO_4 + 3Ca(OH)_2 \rightarrow 6H_2O + Ca_3(PO_4)_2$$

In every reaction of this kind, the products are water and a salt, and it should be recognized that, whereas the identity of the salt is dependent upon the acid and base employed, *water is produced in every case.* **The formation of water** (and a salt) **by the interaction of an acid and a base is known as neutralization.** Even the insoluble bases react with acids provided the salt produced is soluble, thus,

$$3HCl + Fe(OH)_3 \rightarrow 3H_2O + FeCl_3$$

The insoluble oxide Fe_2O_3 does not react extensively with water but is dissolved readily in acids, probably because the acid neutralizes the

protective coating of $Fe(OH)_3$ on the surface of the insoluble oxide and thus permits further reaction between it and water.

That the essential reaction involved in neutralization is the formation of water may be shown by a study of the energy changes involved. Reactions of neutralization are exothermal. If one measures the heat evolved in a large number of neutralization reactions between dilute solutions of different acids and different bases, in every case the quantity of heat evolved upon formation of 1 mole of water is found to be approximately 13,700 cal. This indicates that the heat of reaction is essentially independent of the nature of the salt produced and is related only to the formation of water from the hydrogen of the acid and the hydroxyl radical of the base.

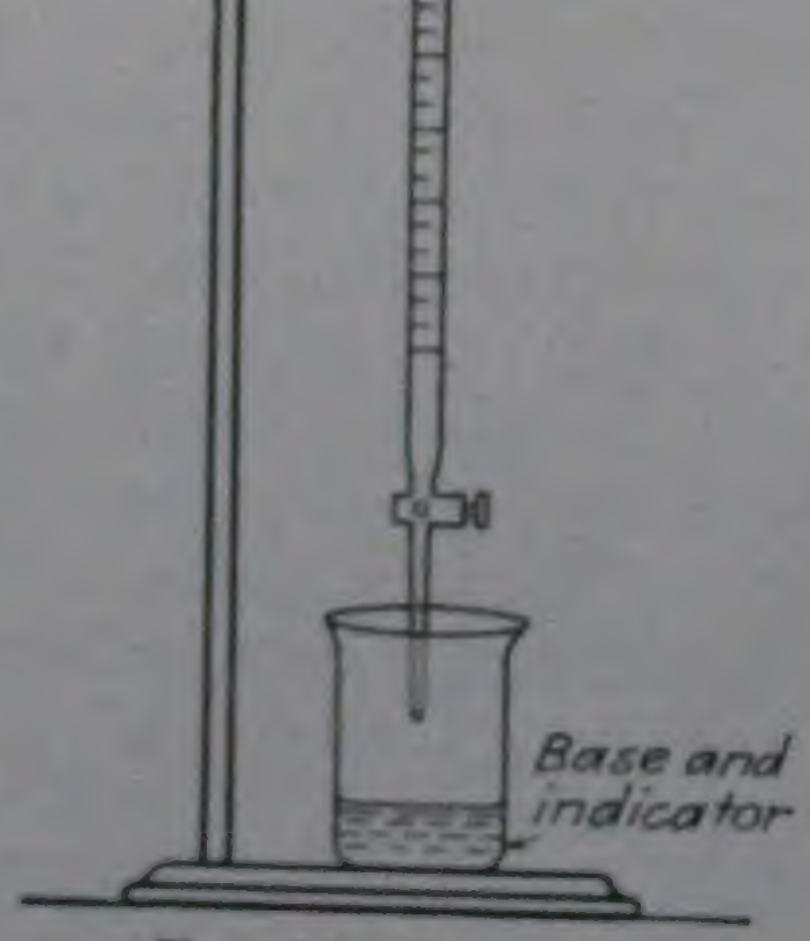

FIG. 66. Titration.

Titration. The chemist frequently has need to determine the volume of one solution required to react with a given volume of another solution. This procedure is known as *titration*, and one is said to *titrate* the one solution against the other. For example, a titration involving a neutralization reaction may be carried out as follows: A known volume of a solution of a base is placed in a beaker and to this solution is added a few drops of a solution of litmus. If a solution of an acid is added from a burette (Fig. 66), the base is neutralized by the acid, but the color of the solution remains blue as long as any of the base remains. Finally, when all of the base has been neutralized and a very slight excess of acid has been added, the color of the solution changes from blue to red. Because the color change is used to denote the end of the neutralization reaction, the dye is called an *indicator* and the occurrence of the color change is referred to as the *end point* of the titration. When one knows the concentration of the acid solution and the volume of acid solution required to neutralize a given volume of the base, the weight of base neutralized and the weights of water and salt formed in the reaction can be calculated.

12.4. Salts

The formation of salts has been shown to result from (1) reactions between metals and acids, (2) reactions between metals and bases, and (3) reactions between acids and bases. Salts constitute one of the most common and useful classes of chemical substances. Other methods by means of which the formation of salts may be accomplished are (4) reactions between acid anhydrides and basic oxides, *e.g.*,

$$CO_2 + CaO \rightarrow CaCO_3$$

(5) reactions between salts and acids, *e.g.*,

$$2NaBr + H_2SO_4 \rightarrow 2HBr + Na_2SO_4$$

and (6) reactions between salts. This latter method is one of unusual importance and is considered in more detail as the need for this information arises in later chapters. The following is a typical example:

$$CaCl_2 + Na_2SO_4 \rightarrow CaSO_4 + 2NaCl$$

Here it is evident that two salts react to form two other salts.

Thus far, definitions of the terms *acid*, *base*, and *salt* have not been formulated. To define these terms (and for that matter the term *neutralization* as well) in a most satisfactory manner requires more information concerning the condition in which acids, bases, and salts exist in solution. The study of the theory of ionization (Chap. 14) provides the necessary information. In the meantime, the student should think of these classes of compounds in terms of their properties and their mode of formation, and in relation to reactions in which these substances participate.

12.5. Amphoteric Bases

There are a few common bases, notably $Sn(OH)_2$, $Pb(OH)_2$, and $Al(OH)_3$, which behave either as bases or as acids depending upon the nature of the environment into which they are placed. If, for example, $Sn(OH)_2$ is brought into the presence of a strong acid such as hydrochloric, the hydroxide acts as a base,

$$\underset{\text{Base}}{Sn(OH)_2} + \underset{\text{Acid}}{2HCl} \rightarrow \underset{\text{Water}}{2H_2O} + \underset{\text{Salt}}{SnCl_2}$$

If, on the other hand, the same compound is brought into the presence of a strong base such as sodium hydroxide, the $Sn(OH)_2$ acts as an

acid, and its formula is accordingly rewritten in a manner that emphasizes its acidic character, *i.e.*, H_2SnO_2.

$$\underset{\text{Acid}}{H_2SnO_2} + \underset{\text{Base}}{NaOH} \rightarrow \underset{\text{Water}}{H_2O} + \underset{\text{Acid salt}}{NaHSnO_2}$$

Further reaction with the strong base converts the acid salt to the normal salt,

$$\underset{\text{Acid salt}}{NaHSnO_2} + \underset{\text{Base}}{NaOH} \rightarrow \underset{\text{Water}}{H_2O} + \underset{\text{Normal salt}}{Na_2SnO_2}$$

This dual role that may be assumed by compounds whose formulas are most commonly represented as bases suggests that acidic and basic characteristics are relative rather than absolute. The importance of this feature of the chemistry of acids and bases is more apparent in relation to the equilibria which exist in ionic solutions (Sec. 15.4).

NOMENCLATURE

It is unfortunate that the names assigned to chemical compounds often fail to conform to any consistent scheme of nomenclature. All too frequently, common or wholly trivial names lacking in chemical significance are employed. Ideally, the name of a compound should convey at least the information required to write the formula. The nomenclature of acids, bases, and salts is fairly consistent, but the exceptions to the general rules of nomenclature are numerous.

12.6. Nomenclature of Binary Compounds

In general, the names of binary compounds (other than binary acids) are constructed from the names of the two elements involved. Since the symbol for the more metallic of the two elements is ordinarily written first in the formula, the name of that element logically is used as the first part of the name of the compound. The second part of the name of the compound consists of the stem of the name of the less metallic element together with the suffix *-ide*. Thus, the compound CaO has the systematic name calcium oxide [*i.e.*, calcium + (oxygen − ygen + ide)]. Similarly, the compound $PbCl_2$ is called lead chloride [*i.e.*, lead + (chlorine − ine + ide)].

In devising names for compounds of the nonmetals (and to some extent those of the metals as well), it often becomes necessary to indicate in the name of the compound the number of atoms of at least one variety of element present in the molecule. This may be done con-

veniently by the use of suitable prefixes. For example, the name carbon oxide is itself inadequate since it might refer equally well to CO or CO_2. Consequently, the names carbon *mon*oxide and carbon *di*oxide, respectively, are employed. Similarly, the compounds PCl_3 and PCl_5 are called phosphorus *tri*chloride and phosphorus *penta*chloride, respectively.

Particularly among binary compounds of the metals (and less frequently in the cases of certain compounds of the nonmetals) the names are so written as to indicate the oxidation state of the more metallic of the two elements. Such a scheme becomes necessary where two elements form more than one compound. For example, consider the case of the two compounds Hg_2O and HgO. In such cases, the names are formed by appending to the name of the more metallic element the suffix *-ous* in the case of the compound in which the more metallic element exhibits the lower oxidation state, and, to indicate the higher oxidation state, the suffix *-ic* is appended similarly. Thus, Hg_2O is called mercur*ous* oxide and HgO is named mercur*ic* oxide. Similarly, $FeCl_2$ and $FeCl_3$ are called ferr*ous* chloride and ferr*ic* chloride, respectively.

It is indeed unfortunate that, in the past, chemists have not expended greater effort in the direction of systematization of nomenclature. There are very many exceptions to the foregoing rules. For example, the compound ammonia is almost always represented by an incorrectly written formula and an unsystematic name. Chemists, by habit, write the formula NH_3 and use the trivial name ammonia, whereas the formula should be written H_3N and the systematic name trihydrogen nitride should be employed.

12.7. Nomenclature of Bases

The naming of bases is a relatively simple matter. The name of a base is formed from the name of the metal (or the radical in the case of a base such as NH_4OH) together with the term *hydroxide*. Thus, NaOH is sodium hydroxide, $Cu(OH)_2$ is copper hydroxide, NH_4OH is ammonium hydroxide, etc. It is unfortunate that the names of these ternary compounds end in *-ide*, a suffix which otherwise is used only in the names of binary compounds.

12.8. Nomenclature of Acids

The scheme generally followed in naming acids is somewhat more involved and requires that distinction be made between binary and ternary acids.

Binary Acids. The names of binary acids consist of the prefix *hydro-*, all or part of the name of the nonmetal, and the suffix *-ic*. For example, the binary acid containing bromine (HBr) is hydrobromic acid (hydro + brom + ic); that containing sulfur (H_2S) is hydrosulfuric acid (hydro + sulfur + ic). The names for the other binary acids are derived similarly.

Ternary Acids. The naming of these acids is complicated by the fact that one nonmetal may be the key element in more than one ternary acid. In such cases, the name of the most common acid is formed from all or part of the name of the nonmetal together with suffix *-ic* (but without the prefix *hydro-*, which is used only in the names of binary acids). Common examples are

H_2SO_4, sulfuric acid (sulfur + ic)

$HClO_3$, chloric acid (chlor + ic)

and

HNO_3, nitric acid (nitr + ic)

Should there be corresponding acids containing one less atom of oxygen, the names are formed in the same manner but employ the suffix *-ous* in place of *-ic*, thus,

H_2SO_3, sulfurous acid (sulfur + ous)

$HClO_2$, chlorous acid (chlor + ous)

and

HNO_2, nitrous acid (nitr + ous)

This scheme is adequate unless still more acids containing the key element are known. In addition to $HClO_3$ and $HClO_2$, the acids having the formulas HClO and $HClO_4$ also are known. It should be noted that $HClO_4$ contains 1 atom of oxygen *more than* the acid having a name ending in *-ic*. Accordingly, this is designated by appending the prefix *per-*, and the name of $HClO_4$ becomes perchloric acid (per + chlor + ic). Similarly, the acid HClO contains 1 atom of oxygen *less than* does that having the name ending in *-ous*, and this information is incorporated in the name by using the prefix *hypo-*. Hence, the name is hypochlorous acid (hypo + chlor + ous).

12.9. Nomenclature of Salts

Salts are named in relation to the acids from which they are derived. The names of binary salts consist of the name of the metal, the stem of the name of the nonmetal other than oxygen, and the suffix *-ide* (Sec.

12.6). On this basis, NaBr is called sodium bromide; AlF_3 is aluminum fluoride; CdS is cadmium sulfide, etc.

Ternary salts are assigned names which incorporate the name of the metal and which otherwise conform to the following rules: (1) If the name of the parent acid ends in *-ic*, the name of the salt must end with the suffix *-ate*. (2) If the name of the acid ends in *-ous*, the name of the salt must end with the suffix *-ite*. (3) If the name of the parent acid ends in *-ic* or *-ous* and involves a prefix such as *per-* or *hypo-*, the prefix is retained in the name of the salt. The application of these rules to the naming of the sodium salts derived from the four ternary acids of chlorine is shown in Table 15.

TABLE 15
NOMENCLATURE OF SALTS

Acid		Salt	
Formula	Name	Formula	Name
HClO	Hypochlorous acid	NaClO	Sodium hypochlorite
$HClO_2$	Chlorous acid	$NaClO_2$	Sodium chlorite
$HClO_3$	Chloric acid	$NaClO_3$	Sodium chlorate
$HClO_4$	Perchloric acid	$NaClO_4$	Sodium perchlorate

Another practice commonly encountered in the naming of salts is the use of the prefix *bi-*, *e.g.*, sodium bicarbonate ($NaHCO_3$). This prefix should not be used at all in the names of inorganic salts of the type represented by $NaHCO_3$, and a means of avoiding its use is given elsewhere (Sec. 14.9).

12.10. An Improved System of Nomenclature

The need for a better system of naming inorganic compounds has long been recognized. This need was met in part in 1940 when a committee representing the chemists of several different countries recommended an improved system for the nomenclature of both simple and complex inorganic compounds. Since these rather extensive recommendations were made, there has been increasing evidence of general adoption and use of these particular rules.

Since a comprehensive discussion of the general problem of nomenclature is beyond the scope of this book, the present discussion is limited to the new scheme for the naming of simple binary and ternary compounds.

Certain types of simple binary compounds are named in a manner such that the number of each kind of atom in the molecule is designated by Greek numerical prefixes in all cases except that in which the number is one. The names given below for the oxides of nitrogen serve to illustrate the method and show that the formula may be written directly on the basis of the systematic name.

Name	Formula
Dinitrogen oxide	N_2O
Nitrogen oxide	NO
Dinitrogen trioxide	N_2O_3
Nitrogen dioxide	NO_2
Dinitrogen tetroxide	N_2O_4
Dinitrogen pentoxide	N_2O_5

Other simple binary compounds may be named similarly, and many of the names already in use conform to this system, *e.g.*, carbon monoxide, carbon dioxide, iron disulfide, etc. Ternary compounds may be named similarly, provided they are composed of one element and a radical having an established name.

Certain other types of binary, ternary, and quaternary compounds are given names that include designations of oxidation state wherever necessary, *i.e.*, for elements that exhibit more than one oxidation state. The oxidation state is shown by Roman numerals placed in parentheses immediately following the name of the element in question. The accompanying formulas and the corresponding systematic names serve as illustrations.

Formula	Name
FeO	Iron(II) oxide
Fe_2O_3	Iron(III) oxide
Fe_3O_4*	Iron(II,III) oxide
$CrCl_3$	Chromium(III) chloride
$Hg(NO_3)_2$	Mercury(II) nitrate
$Pb(C_2H_3O_2)_4$	Lead(IV) acetate

* This formula may also be written as $FeO \cdot Fe_2O_3$.

It is not necessary to designate the state of elements that seldom exhibit more than one oxidation state, *e.g.*, Al, Zn, Ca, Na, K, etc.

It should be noted that the foregoing examples do not involve the use of suffixes such as *-ous* and *-ic*. According to this system of nomenclature, these and similar suffixes are not used except in the naming of acids.

In the remainder of this book, only infrequent reference is made to this system of nomenclature. However, it is felt that the student

should be aware of the fact that inorganic nomenclature is presently undergoing a transition to more systematic practices. This is particularly important for those students who expect to continue with the study of chemistry.

12.11. Quantitative Aspects of Neutralization

One liter of 1 *M* hydrochloric acid solution neutralizes 1 liter of 1 *M* sodium hydroxide solution because the two solutions contain solutes (HCl and NaOH, respectively) in the quantities required by the following equation:

$$\underset{36.5\text{ g.}}{HCl} + \underset{40\text{ g.}}{NaOH} \rightarrow H_2O + NaCl$$

That is, the neutralization reaction is not a reaction of the solution as such, but rather is one that depends upon the identity and properties of the solutes. Reactions of neutralization occur in relation to the H and OH content of the acidic and basic solutions, respectively. Accordingly, molar and molal solutions are not convenient standard solutions for use in reactions of neutralization. For example, 1 liter of a 1 *M* solution of H_2SO_4 contains 2.016 g. of replaceable H and can therefore neutralize 2 liters of 1 *M* sodium hydroxide solution, each liter of which contains 17.008 g. of OH, since

$$\underset{1.008\text{ g.}}{H} + \underset{17.008\text{ g.}}{OH} \rightarrow \underset{18.016\text{ g.}}{H_2O}$$

This situation suggests a need for a kind of standard solution which is related directly to the particular chemical individuals involved in the fundamental chemical changes in which these solutions are to be employed. *Normal solutions* are defined, prepared, and used in accordance with this point of view.

Normal Solutions of Acids. A normal solution of an acid is one that contains 1 gram atom of replaceable hydrogen (1.008 g.) per liter of solution. On this basis, a specified volume of a 1 *N* solution of *any* acid contains the same weight of replaceable hydrogen as the same volume of 1 *N* solution of any other acid. This relation may be clarified by consideration of the following examples. Suppose that it is desired to prepare 1 liter of 1 *N* solution of each of the acids HCl, H_2SO_4, and H_3PO_4. The weight of solute required in each case is

(*a*) HCl: Mol. wt. = 36.465 g., of which 1.008 g. is hydrogen. Consequently, 36.465 g. of HCl dissolved in enough water to make 1 liter of solution provides a solution containing the exact weight of replaceable H required by the definition of a normal solution of an acid.

(*b*) H_2SO_4: Mol. wt. = 98.076 g., containing 2.016 g. of replaceable hydrogen. If 98.076 g. of H_2SO_4 were dissolved in enough water to make 1 liter of solution, the resulting solution would be 2 *N* since it would contain 2 gram atoms of replaceable hydrogen. Accordingly, $98.076 \div 2 = 49.038$ g. of H_2SO_4 is the required weight of solute per liter of 1 *N* solution of sulfuric acid.

(*c*) H_3PO_4: Mol. wt = 98.044 g. Since 1 gram-molecular weight of H_3PO_4 contains 3 gram atoms of replaceable hydrogen, the weight of H_3PO_4 required to prepare 1 liter of 1 *N* phosphoric acid solution is $98.044 \div 3 = 32.682$ g.

Normal Solutions of Bases. A normal solution of a base is one that contains 17.008 g. of available hydroxyl (OH) per liter of solution. In terms of this definition, the weights of potassium hydroxide and barium hydroxide, for example, required to prepare 1 liter of 1 *N* solutions are

(*a*) KOH: Mol. wt. = 56.104 g. Of this weight, 17.008 g. is contributed by the one OH radical. Consequently, 56.104 g. of KOH dissolved in enough water to make 1 liter of solution provides a 1 *N* solution of potassium hydroxide.

(*b*) $Ba(OH)_2$: Mol. wt. = 171.376 g., containing a total of 2×17.008 g. of OH. Hence, $171.376 \div 2 = 85.688$ g. is the weight of $Ba(OH)_2$ required to prepare 1 liter of 1 *N* barium hydroxide solution.[1]

From the preceding examples, it should be apparent that any given volume of any 1 *N* acid solution is chemically equivalent to the same volume of any 1 *N* solution of a base. For example, 50 ml. of a 1 *N* solution of *any* acid contains just exactly the quantity of H required to neutralize the weight of OH contained in 50 ml. of a 1 *N* solution of *any* base. If the acid solution is 2 *N*, then 50 ml. of the 2 *N* acid neutralizes 100 ml. of 1 *N* base. A little reflection upon these and similar cases leads directly to the relationship

$$N_{(\text{acid})} \times V_{(\text{acid})} = N_{(\text{base})} \times V_{(\text{base})}$$

where *N* and *V* represent normality and volume, respectively.

Normal Solutions of Salts. Since the preceding discussion of normal solutions of acids and bases has been wholly in terms of replaceable H and OH, it may not be immediately apparent that it would be possible also to deal with normal solutions of salts, which contain neither H nor OH. In terms of equivalent weights (Sec. 2.2), however,

[1] In fact, barium hydroxide is not sufficiently soluble in water to permit the preparation of a 1 *N* solution of this base. Solutions of lower normality (up to about 0.4 *N*) are possible and are commonly used.

it should be noted that 1.008 g. of hydrogen constitutes 1 gram-equivalent weight of this element. Similarly, 17.008 g. of hydroxyl radical must also constitute 1 gram-equivalent weight of OH, since this is the quantity that combines with 1.008 g. of hydrogen. It follows that one may define any normal solution as one which contains **one gram-equivalent weight of solute in one liter of solution.** This definition obviously embraces the more specific designations given previously for normal solutions of acids and normal solutions of bases; salts also are included.

Before further consideration is given to normal solutions of salts, attention may be given with profit to two more problems concerned with acids and bases. The first problem is: what is the normality of a solution which contains 31.39 g. of H_2SO_4? Since 1 gram-molecular weight of H_2SO_4 contains 2 equivalents of hydrogen, then

$$\text{Gram-equiv. wt. of } H_2SO_4 = \frac{\text{mol. wt. of } H_2SO_4}{2}$$

$$= \frac{98.08}{2}$$

$$= 49.04$$

from which it follows that

$$\text{Normality} = \frac{\text{wt. present}}{\text{equiv. wt.}}$$

$$= \frac{31.39}{49.04}$$

$$= 0.64$$

Consider also the following type of problem: How many gram-equivalent weights of $Ca(OH)_2$ are contained in 200 ml. of 0.04 N calcium hydroxide solution?

$$\text{Gram-equiv. wt. of } Ca(OH)_2 = \frac{\text{mol. wt. of } Ca(OH)_2}{2}$$

$$= \frac{74.096}{2}$$

$$= 37.048$$

This is the weight of solute that would be present in 1 liter of 1 N calcium hydroxide solution. The weight present in 200 ml. of 0.04 N solution would therefore be

$$37.048 \times {}^{200}\!/_{1000} \times 0.04 = 0.296 \text{ g.}$$

and, since 1 gram-equivalent weight of calcium hydroxide is 37.048.

then

$$\text{Number of equivalents} = \frac{0.296}{37.048}$$

$$= 0.008$$

Normal solutions of salts are considered on exactly the same basis. For example, the molecular weight of the salt K_3PO_4 is 212.27. One gram-equivalent weight of potassium phosphate must therefore be $212.27 \div 3 = 70.76$ g., since this quantity represents 1 equivalent of either potassium or phosphate radical. Consequently, 70.76 g. of K_3PO_4 is the weight required to prepare 1 liter of 1 *N* potassium phosphate solution.

Although normal solutions of salts are sometimes used, they are certainly less common than normal solutions of acids and bases.

Preparation of Normal Solutions. Since solutions that are 1 *N* are usually too concentrated for most purposes, it is more suitable to prepare 0.5 *N*, 0.1 *N*, 0.01 *N*, or solutions of any convenient normality. In order to illustrate the procedure involved in the preparation of a given volume of a solution of some specified normality, suppose that one requires 700 ml. of 0.2 *N* sulfuric acid solution. The first problem is that of calculating the weight of pure hydrogen sulfate required. 1 liter of 1 *N* sulfuric acid solution requires

$$\frac{98.076}{2} = 49.038 \text{ g. } H_2SO_4$$

1 liter of 0.2 *N* sulfuric acid solution requires

$$49.038 \times 0.2 = 9.8076 \text{ g. } H_2SO_4$$

700 ml. of 0.2 *N* sulfuric acid solution requires

$$9.8076 \times \frac{700}{1000} = 6.8653 \text{ g. } H_2SO_4$$

Next, one would weigh out exactly 6.8653 g. of pure H_2SO_4, dissolve it in water contained in a flask of suitable size, then add just enough water to make a total volume of exactly 700 ml. of solution.

GENERAL EXERCISES

1. Define the following terms: (*a*) acid anhydride, (*b*) neutralization, (*c*) titration, (*d*) indicator, (*e*) end point.
2. What is the formula of the anhydride of chromic acid (H_2CrO_4), of arsenic acid (H_3AsO_4), of perchloric acid?
3. Show by means of an equation that chlorine dioxide (ClO_2) is at the same time the anhydride of both chlorous and chloric acids.
4. Write equations to represent the reactions that occur between the following:

(*a*) Calcium hydroxide and sulfuric acid
(*b*) Bismuth hydroxide and hydrochloric acid
(*c*) Magnesium hydroxide and acetic acid
(*d*) Lead hydroxide and phosphoric acid
(*e*) Zinc hydroxide and hydrobromic acid
(*f*) Potassium hydroxide and hydriodic acid
(*g*) Barium hydroxide and chloric acid

5. Write systematic names for each of the following simple binary compounds:

(*a*) SCl_2
(*b*) P_2O_5
(*c*) $SiBr_4$
(*d*) PbO_2
(*e*) Na_2S_4
(*f*) As_2O_3

6. Of the following known oxides of nitrogen, N_2O is commonly called nitrous oxide and NO is known as nitric oxide. Assuming, however, that the suffixes *-ous* and *-ic* are not to be used at all, assign suitable systematic names for the following: N_2O, NO, NO_2, NO_3, N_2O_3, N_2O_5.

7. From the following names, write the corresponding formulas:

(*a*) Dipotassium tetroxide
(*b*) Stannous iodide
(*c*) Plumbous oxide
(*d*) Mercuric sulfide
(*e*) Silicon dioxide
(*f*) Iron(II) oxide
(*g*) Arsenic(V) sulfide
(*h*) Bismuth(III) chloride

8. Write systematic names for the following salts:

$SbBr_3$
$Al_2(SO_4)_3$
$AgClO_4$
Na_2SO_4
$Cu(NO_3)_2$
$Cd_3(PO_4)_2$
$Zn(ClO_3)_2$
FeI_3
$Mn(NO_2)_2$
$KClO_2$
$Ca(ClO)_2$
$Sn_3(PO_3)_2$

9. From the following names, write the corresponding formulas:

Nickel sulfate
Strontium fluoride
Barium chlorite
Magnesium perchlorate
Lead acetate
Zinc phosphate
Sodium phosphite
Silver hypochlorite

PROBLEMS

1. Find the weight of solute required to prepare the following solutions:

(*a*) 2 liters of 0.1 *N* phosphoric acid solution
(*b*) 500 ml. of 4 *N* potassium hydroxide solution
(*c*) 200 ml. of 0.06 *N* perchloric acid solution
(*d*) 8 liters of 0.8 *N* hydrobromic acid solution
(*e*) 1.5 liters of 1 *N* sodium chloride solution
(*f*) 100 ml. of 0.1 *N* lead nitrate solution

2. Find the weight of solute contained in each of the following solutions:

(*a*) 1 liter of 0.2 *N* hypochlorous acid solution
(*b*) 16 liters of 0.003 *N* ammonium hydroxide solution
(*c*) 50 ml. of 6 *N* sulfuric acid solution

(*d*) 1 ml. of 0.75 *N* hydriodic acid solution
(*e*) 100 ml. of 0.5 *N* copper sulfate solution
(*f*) 3.5 liters of 0.001 *N* trisodium phosphate solution

3. What is the normality of (*a*) 1 *M* sulfuric acid solution, (*b*) 0.5 *M* sodium hydroxide solution, (*c*) 2 *M* phosphoric acid solution?

4. Calculate (*a*) the molarity and (*b*) the normality of a solution that contains 16.22 g. of ferric chloride in 50 ml. of solution.

5. What is the normality of solutions that contain:
(*a*) 266.68 g. of $AlCl_3$ in 2 liters of solution
(*b*) 15.76 g. of HNO_3 in 1 liter of solution
(*c*) 171.1 g. of $Al_2(SO_4)_3$ in 500 ml. of solution

6. What volume of 0.001 *N* hydrosulfuric acid solution would be equivalent to 0.66 ml. of 0.024 *N* hydrobromic acid solution?

7. In a titration, 26 ml. of 0.4 *N* sulfuric acid solution was required exactly to neutralize 38 ml. of a barium hydroxide solution.
(*a*) Calculate the *weight* of $Ba(OH)_2$ contained in the 38 ml. of barium hydroxide solution.
(*b*) Using *only* the weight of solute (calculated above) and the volume of 38 ml., calculate the normality of the barium hydroxide solution.
(*c*) Calculate the normality of the barium hydroxide solution using the relationship given in Sec. 12.11.

8. How many grams of $Zn(NO_3)_2$ are required to prepare 150 ml. of 0.5 *N* solution?

9. For use in a certain reaction there is required exactly 0.95 equivalent of potassium iodide. If a stock solution of 2 *N* KI is available, how many milliliters of this solution should be used?

10. How many gram-equivalent weights of ammonium sulfite are contained in (*a*) 100 ml. of 1.5 *N* solution, (*b*) 30 ml. of 0.8 *N* solution?

11. To what volume must 56 ml. of 0.16 *N* sodium hydroxide solution be diluted to reduce the normality to 0.008?

12. What volume of water must be added to 112 ml. of 0.18 *N* hydrochloric acid solution in order to lower the normality to 0.0075?

13. Eighty-five milliliters of 0.7 *N* hydrochloric acid solution was diluted until the solution was 0.046 *N*. What volume of water (in liters) was added?

14. One liter of 2.24 *N* sodium sulfate solution was evaporated until the normality of the solution was increased to 2.80. How many milliliters of water were removed during the evaporation process?

15. A lump of solid pure calcium oxide was placed in water and neutralized by the addition of 60 ml. of 2.4 *N* hydrochloric acid solution. Without the use of any typical calculations based upon chemical equations, calculate the *weight* (in grams) of the lump of calcium oxide.

SUGGESTED READING[1]

Journal of Chemical Education

Beezer, Latin and Greek Roots in Chemical Terminology, **17**, 63 (1940).
Ewing, What's in a Name?, **15**, 123 (1938).

[1]See also references at end of Chap. 15.

SEIDELL, Limitations upon the Unification of Chemical Nomenclature, **6**, 720 (1929).

Chemical Reviews

SCOTT, The Need for Reform in Inorganic Chemical Nomenclature, **32**, 73 (1943).

Journal of the American Chemical Society

JORISSEN, BASSETT, DAMIENS, FICHTER, and REMY, Rules for Naming Inorganic Compounds, **63**, 889 (1941).

CHAPTER 13

REVERSIBLE REACTIONS AND CHEMICAL EQUILIBRIUM

The idea of two processes occurring simultaneously but in opposite directions is not a new one. Such related processes have been seen to be involved when a volatile liquid such as water is in contact with water vapor in a closed vessel (Sec. 7.5),

$$H_2O_{(liquid)} \rightarrow H_2O_{(vapor)}$$

while, at the same time,

$$H_2O_{(vapor)} \rightarrow H_2O_{(liquid)}$$

Similarly, when a saturated solution of sugar exists in contact with undissolved solute (Sec. 10.4),

$$C_{12}H_{22}O_{11(solid)} \rightarrow C_{12}H_{22}O_{11(dissolved)}$$

and

$$C_{12}H_{22}O_{11(dissolved)} \rightarrow C_{12}H_{22}O_{11(solid)}$$

These processes may be represented each by a single expression,

$$H_2O_{(liquid)} \rightleftharpoons H_2O_{(vapor)}$$

$$C_{12}H_{22}O_{11(solid)} \rightleftharpoons C_{12}H_{22}O_{11(dissolved)}$$

Here the double arrows simply indicate that the conversion of liquid water to water vapor and the change from solid sugar to dissolved sugar are reversible processes. Although these two examples are concerned entirely with physical changes, they suggest that similar situations may be anticipated among chemical transformations.

13.1. Reversible Reactions

In Sec. 3.3, the formation of water was represented by the equation,

$$2H_2 + O_2 \rightarrow 2H_2O$$

In Secs. 5.1 and 9.6, the decomposition of water was given as a method for the preparation of oxygen and hydrogen, respectively.

$$2H_2O \rightarrow 2H_2 + O_2$$

These two equations may be combined into a single expression,

$$2H_2 + O_2 \rightleftharpoons 2H_2O$$

which provides the information that the union of hydrogen and oxygen is a reversible chemical reaction and that the formation and decomposition of water may occur at the same time. If the rate of formation of water is the same as the rate of decomposition, the two chemical reactions exhibit that balance of opposing tendencies which is known as a *state of dynamic equilibrium.*

Another example of a reversible reaction has been encountered previously. The formation of hydrogen by the reaction,

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

and the reduction of magnetic oxide of iron by means of hydrogen,

$$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O$$

are also seen to constitute a reversible system which may be represented by the single equation,

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

A reversible chemical reaction is one that is capable of proceeding in either of two directions. In referring to systems of this sort, the chemist speaks of the reaction represented by the arrow pointing toward the right as "the forward reaction," and that represented by the arrow pointing toward the left as "the reverse reaction."

Most chemical reactions are reversible. There are, however, many reactions that can hardly be thought of properly as reversible processes. It would be difficult indeed, if not impossible, to find experimental conditions that would make possible the complete reversal of the processes involved in the burning of a fuel such as coal, the decomposition of sugar by means of heat, the digestion of foodstuffs of complex composition, etc. It is wholly conceivable that all chemical changes are reversible and that the chemist's inability to bring about the reversal of some of these complex reactions is only the result of inadequate knowledge.

13.2. Rates of Reaction

The study of reversible reactions that reach a condition of equilibrium is largely concerned with the investigation of the comparative rates of two opposing reactions. With reference to chemical changes, the term *rate* (or velocity, or speed) has to do with the quantity of

material undergoing chemical transformation in unit time. The production of crude petroleum is expressed in terms of barrels per day. In an entirely analogous manner, the chemist speaks of the decomposition of potassium chlorate as proceeding at a rate of 0.1 g. per sec., or 1 mole per hr., etc.

13.3. Approach to a Condition of Dynamic Equilibrium

Before proceeding to any detailed study of specific cases, it is helpful to attempt to visualize the sequence of events leading to the establishment of a state of dynamic equilibrium. This may be done in a general way without reference to any particular reaction, and the resulting mental picture is equally applicable to both physical and chemical equilibria.

Suppose that two substances, A and B, react to form two other substances, C and D, and that the reaction is reversible.

$$A + B \rightleftharpoons C + D$$

If 1 mole of A and 1 mole of B are brought together, the forward reaction is the only one that can occur initially because some of C and D must be formed before the reverse reaction can occur at all. Initially, the rate of reaction between molecules of A and B is rapid because there are many of these molecules present and they collide (and react) frequently. However, as the available molecules of A and B are used up, the frequency of collision decreases and the rate of the forward reaction becomes slower and slower. Also, molecules of A and B collide not only with each other but with themselves and with other molecules present, *e.g.*, molecules of the products C and D. Consequently the probability of collisions between A and B decreases as the number of other kinds of molecules present increases. In the meantime, the available number of molecules of C and D has been increasing steadily, and this in turn permits the rate of the reverse reaction to increase in proportion. So, while the rate of the forward reaction steadily decreases, the rate of the reverse reaction steadily increases. Finally, the rates of the two opposing reactions become equal, and the two reactions continue to occur without any further net gain in either direction. The reactions have then arrived at a condition of dynamic equilibrium.

13.4. Completion of Reactions

In their practical applications either for small-scale laboratory use or in commercial use, reactions are usually carried out for the purpose

of producing some desired product or combination of products. Advantage is taken of the union of nitrogen and hydrogen in the synthesis of ammonia,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

but, as is indicated by the equation, the reaction is reversible and reaches a condition of equilibrium. In this or in any similar case, the problem faced by the chemist is that of determining how much of the desired product can be formed before equilibrium is established. In

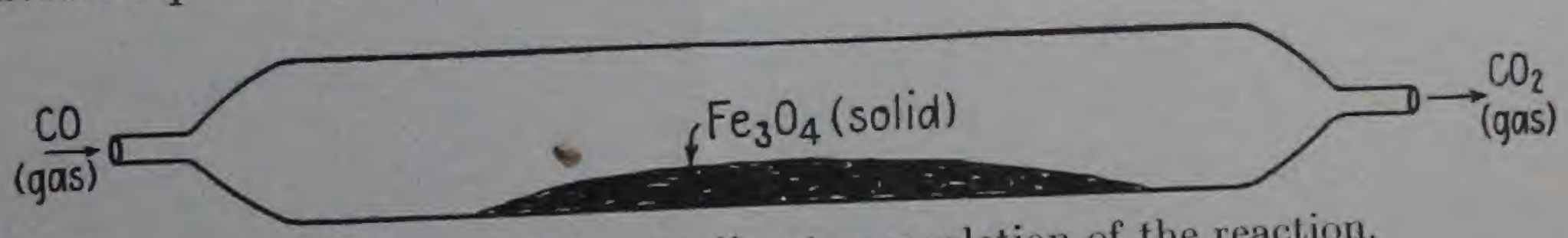

FIG. 67. Conditions leading to completion of the reaction.

other words, it is desired to cause one reaction to proceed as nearly as possible to completion.

Reactions that otherwise would come to a state of equilibrium may be caused to go to completion by removing one of the products of the be caused to go to completion by removing one of the products of the reaction. The production of iron on an industrial scale may be represented by the reversible reaction,

$$Fe_3O_4 + 4CO \rightleftharpoons 3Fe + 4CO_2$$

If this reaction is carried out in an apparatus of the type shown in Fig. 67, the forward reaction may be caused to go to completion. The CO_2 which is formed in the forward reaction is removed and is, of course, unable to come into contact with the Fe and thereby participate in the reverse reaction. By this arrangement the reverse reaction is elimi-

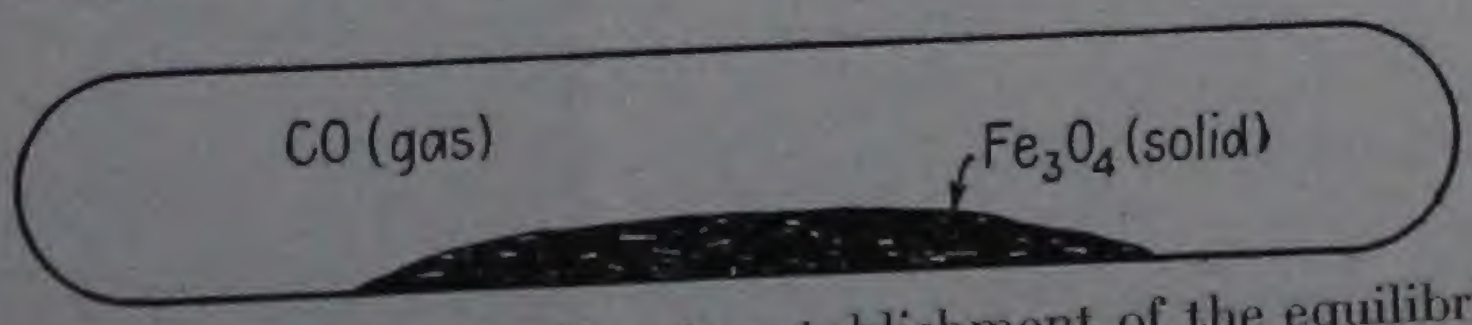

FIG. 68. Conditions leading to establishment of the equilibrium.

nated by keeping apart those reactants which are necessary for the occurrence of the reverse reaction. If, on the other hand, it was necessary for some reason to carry out this reaction in a closed vessel (Fig. 68), a state of equilibrium could not be avoided. Under these conditions, net gain in the direction of the formation of iron can be realized only until the two reactions reach equilibrium unless ways can be found to influence the rate of the forward reaction at the expense of the reverse reaction.

13.5. Methods of Expressing Concentration

From the point of view of the kinetic-molecular theory, the occurrence of a chemical reaction depends upon collisions between molecules of the reacting substances. The *total weight* of a given reactant is therefore less important than is the *total number of available molecules*. Although it is not convenient to deal with figures representing the actual number of molecules contained in any chosen unit of volume, the same purpose is accomplished by expressing concentration in terms of gram-molecular weights (or moles) since a mole of any substance represents a definite number of molecules (6.02×10^{23} molecules).

Suppose, for example, that 22 g. of hydrogen gas is placed in a 1-liter flask and that 22 g. of oxygen is contained in another 1-liter flask. In terms of weight per unit volume, the concentrations of hydrogen and oxygen (denoted by C_{H_2} and C_{O_2}, respectively) are

$$C_{H_2} = 22 \text{ g. per } 1000 \text{ ml.}$$

$$= 0.022 \text{ g. per ml.}$$

$$C_{O_2} = 22 \text{ g. per } 1000 \text{ ml.}$$

$$= 0.022 \text{ g. per ml.}$$

In terms of *molecular concentration*, denoted by $[H_2]$ and $[O_2]$, respectively, the concentrations of hydrogen and oxygen are

$$[H_2] = \frac{22 \div 2.016}{1000}$$

$$= 0.01091 \text{ mole per ml.}$$

$$[O_2] = \frac{22 \div 32}{1000}$$

$$= 0.0007 \text{ mole per ml.}$$

Thus, it is apparent that the number of moles per unit of volume is markedly different in the two cases even though the weight per unit of volume is the same. Whenever concentrations are expressed by symbols or formulas enclosed by brackets, molecular concentrations are indicated. An expression such as $[H_2]$ is read "the molecular concentration of hydrogen."

Concentration of Solids. For reactions concerned only with gases, it is easy to see why it might be advantageous to speak in terms of molecular concentration. In a mixture of gases, the molecules can move about and come into contact with molecules of the other reac-

tant, *i.e.*, the molecules of a gas are all readily *available* for reaction, and the number of molecules present per unit of volume governs the probability of reaction. With solids, however, the situation is vastly different. Reaction can occur only at the surface of solids, *i.e.*, only where the molecules of the solid are exposed (available). If a solid lump of sulfur is allowed to react with oxygen gas to form sulfur dioxide,

$$O_2 + S \rightarrow SO_2$$

reaction can occur only on the exposed surface of the lump of solid sulfur. Initially, the sulfur is present at a definite concentration expressed either as grams per unit of volume or gram atoms per unit of volume. As the reaction proceeds, the size of the lump of sulfur decreases; both the total weight of sulfur and the total volume occupied by solid sulfur diminish, but *the quantity of sulfur per unit volume of solid sulfur remains the same.* For this reason, the concentration of a solid substance is said to remain constant.

13.6. Law of Mass Action

The manner in which the rates of reactions are influenced by concentration is described by the law of mass action, which may be stated as follows: **The rate of a chemical reaction is directly proportional to the product of the molecular concentrations of the reactants.** Consider the reaction,

$$H_2 + Cl_2 \rightleftharpoons 2HCl$$

If 500 molecules of hydrogen and 500 molecules of chlorine are brought together at a suitable temperature in a closed container, the formation of HCl occurs, and an equilibrium is established. At equilibrium, the $[H_2]$ $[H_2]$ and $[Cl_2]$ have definite values in moles per liter. If now the $[H_2]$ is increased by placing in the flask an additional 100 molecules of H_2, the chance that any given chlorine molecule will collide with a hydrogen molecule is certainly enhanced. As a result of this change (increase) in the molecular concentration of hydrogen, more HCl is formed, less Cl_2 is present, and in time a new equilibrium becomes established. At this new set of equilibrium conditions, however, more HCl has been produced than was formed at the time the original equilibrium was established. Thus, it may be said that by increasing the molecular concentration of one of the reactants, the original equilibrium mixture was replaced by a new equilibrium mixture containing more hydrogen chloride and less chlorine. Similarly, by decreasing the molecular concentration of either of the reactants, the original

equilibrium mixture could have been replaced by one containing less hydrogen chloride. If one wished to produce HCl commercially by this reaction and if H_2 were cheap and Cl_2 expensive, it certainly would be profitable to use an excess of H_2 in order to get the maximum possible quantity of HCl from a given quantity of Cl_2.

13.7. Influence of Experimental Conditions upon Reactions in Equilibrium

In any consideration of the effects produced by changes in the conditions imposed upon reactions in equilibrium, it must be kept in mind that all components of the equilibrium mixture are subject to whatever changes are made. The reactants and products are all together as a mixture, and one may not properly think of the effect of a change in temperature, for example, solely in terms of either the reactants or products.

Concentration. The manner in which a change in the concentration of a component of an equilibrium mixture influences the equilibrium situation has been illustrated in the preceding section. For equilibria involving gases, a change in pressure amounts to a change in concentration. An increase in the pressure exerted upon a confined gas causes the molecules to occupy a smaller total volume, and hence there are more molecules per unit volume. The partial pressure of each gas in the equilibrium mixture is increased owing to the increase in pressure, and it is of importance to recognize that the *initial* effect of the change is at least momentarily the same for all gaseous components of the mixture.

The changes that may occur after the initial increase in concentration depend upon the nature of the reactions involved. In the synthesis of ammonia from nitrogen and hydrogen,

$$\underset{\text{1 vol.}}{N_2} + \underset{\text{3 vol.}}{3H_2} \rightleftharpoons \underset{\text{2 vol.}}{2NH_3}$$

it is seen that the nitrogen and hydrogen together occupy a total of four volumes when uncombined, but occupy only two volumes when combined in the form of ammonia. If the four volumes of nitrogen and hydrogen are subjected to an increase in pressure, the gases must occupy a smaller volume. By combining to form ammonia, the two gases are responding chemically to produce the natural physical result of compression, *viz.*, a smaller total volume. Thus, the resulting equilibrium mixture contains relatively more ammonia, a fact that is utilized to advantage in the commercial production of ammonia.

This is only one example of the manner in which reactions in equilib-

rium respond to changes in conditions. A general statement concerning the character of these responses is known as Le Châtelier's law (or principle). **If a system in equilibrium is subjected to any stress or constraint, the system responds in such manner as to counteract the effects produced by the applied stress.** Not only changes in concentration but also changes in temperature constitute "stresses" or "constraints" in the sense that they tend to disturb the established conditions peculiar to a particular equilibrium.

Temperature. If one of the two reactions in equilibrium is exothermal, the other must be endothermal to the same extent. Again using the synthesis of ammonia as an example,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 24{,}500 \text{ cal.}$$

the forward reaction is seen to be exothermal. As a result, the formation of ammonia may be made more complete by removing the heat (one of the products of the forward reaction) produced. If heat is supplied from the outside, the reverse reaction is favored, and this leads to an equilibrium mixture relatively richer in nitrogen and hydrogen.

For an endothermal reaction, an increase in temperature makes a change in the composition of the equilibrium mixture that is favorable to those components formed endothermally and unfavorable to those formed exothermally. Just the reverse is true for a decrease in temperature.

Catalysis. A catalyst can influence an equilibrium situation only in the sense that the catalyst may increase the speed at which equilibrium may be attained, or permit an equilibrium to be established at a lower temperature. Considerable saving may be realized by permitting equilibrium to become established more quickly and at a lower temperature than would be possible in the absence of a catalyst. Not only does this permit the production of a given quantity of product in shorter time, but it also reduces costs because of the lesser heat energy expended.

13.8. Equilibrium Constant

When a reversible reaction is carried out for the purpose of producing a certain product for sale, the success or failure of the venture depends upon the efficiency with which the given reactants can be converted to the desired product or products. It is important, therefore, to have some means of determining experimentally just how closely a reaction approaches completion before equilibrium is established. Consider

again the reaction

$$Fe_3O_4 + 4H_2 \rightleftharpoons 3Fe + 4H_2O$$

Let R_A represent the rate of the forward reaction and R_B the rate of the reverse reaction. By the law of mass action, the rate of each reaction is proportional to the product[1] of the molecular concentrations of the reactants, hence,

$$\begin{aligned} R_A &= k_1 \times [Fe_3O_4] \times [H_2] \times [H_2] \times [H_2] \times [H_2] \\ &= k_1 \times [Fe_3O_4] \times [H_2]^4 \\ R_B &= k_2 \times [Fe] \times [Fe] \times [Fe] \times [H_2O] \times [H_2O] \times [H_2O] \times [H_2O] \\ &= k_2 \times [Fe]^3 \times [H_2O]^4 \end{aligned}$$

where k_1 and k_2 are constants (numbers) which represent the rates at which the two reactions occur when the reactants are present *at unit concentration*. Since the molecular concentration of solids may be considered constant (Sec. 13.5), the terms $[Fe_3O_4]$ and $[Fe]^3$ may be replaced by the constants C and D, respectively.

$$R_A = k_1 \times C \times [H_2]^4$$

or

$$R_A = K_1 \times [H_2]^4$$

and

$$R_B = k_2 \times D \times [H_2O]^4$$

or

$$R_B = K_2 \times [H_2O]^4$$

When equilibrium becomes established at some definite temperature and pressure, the two rates of reaction must be equal, *i.e.*,

$$R_B = R_A$$

Substituting,

$$K_2 \times [H_2O]^4 = K_1 \times [H_2]^4$$

[1] The fact that the rate of reaction is proportional to the *product* of the molecular concentrations is related to the *probability* of collisions between molecules. If dice are being cast and only aces (single dots) are desired, the chance of turning up an ace using only one die is one in six ($\frac{1}{6}$) because the die has six different faces, only one of which has the ace on it. Likewise, the chance that another ace will turn up when a second die is cast is also $\frac{1}{6}$. When two dice are cast, the chance that both will turn up aces *simultaneously* is only 1 in 36, or $\frac{1}{6} \times \frac{1}{6} = \frac{1}{36}$. This must be true because with two dice there are 36 possible face combinations, in which the ace-ace combination appears only once. With regard to chemical reactions, the same line of reasoning applies since the occurrence of a reaction depends upon the probability that the reacting molecules will appear simultaneously in a given location in space.

and

$$\frac{[H_2O]^4}{[H_2]^4} = \frac{K_1}{K_2}$$

$$\sqrt[4]{\frac{[H_2O]^4}{[H_2]^4}} = \sqrt[4]{\frac{K_1}{K_2}}$$

$$\frac{[H_2O]}{[H_2]} = K$$

K is the *equilibrium constant* for this particular reaction in equilibrium under a specified set of experimental conditions. From this example, and from ones that are given later, it is seen that for the earlier statement of the law of mass action to be valid, each concentration term must be raised to a power corresponding to the appropriate coefficient in the chemical equation.

This equilibrium constant is simply a number which represents the ratio of the molecular concentration of H_2O and the molecular concentration of H_2 present when this particular equilibrium becomes established. The numerical value of this ratio is entirely independent of the original proportions in which the reactants are brought together, but it does change with temperature. For this equilibrium at 900°C., $K = 0.69$; at 1025°, $K = 0.78$; and at 1150°, $K = 0.86$. Increase in the numerical value of K means that $[H_2O]$ has increased and $[H_2]$ has decreased with increase in temperature. In other words, increase in temperature produces an equilibrium mixture containing more H_2O (and therefore Fe as well), which is the desired result. The larger the value of the equilibrium constant, the more nearly complete is the forward reaction; by the same token a small numerical value of K indicates that the forward reaction did not proceed very far before equilibrium was established.

13.9. Influence of Changes in Temperature and Concentration upon the Equilibrium Constant

The manner in which changes in temperature and concentration influence the composition of equilibrium mixtures is described in Sec. 13.7. It is important here to make a clear distinction between the effect of these variables upon the *composition of the equilibrium mixture* and upon the *numerical value of the equilibrium constant*.

Consider, for example, the effect of changes in temperature and concentration upon the equilibrium

$$H_{2(gas)} + I_{2(gas)} \rightleftharpoons 2HI_{(gas)}$$

for which there may be written the equilibrium-constant expression

$$\frac{[HI]^2}{[H_2] \times [I_2]} = \frac{k_1}{k_2} = K$$

The equilibrium constant is seen to be the ratio of the specific reaction rate constants k_1 and k_2 for the forward and reverse reactions, respectively, at some definite temperature. If the temperature is changed, the rates of these two reactions are altered. Consequently, k_1 and k_2 change, and K must also change accordingly. Whether k_1 or k_2 increases or decreases with the change in temperature depends upon which reaction is endothermal and which is exothermal. One must therefore conclude that temperature is the only experimental variable that can lead to a change in the numerical value of the equilibrium constant. It is possible that even a change in temperature might not result in any change in K. This could be possible only if the particular change has the same net effect upon the rates of the forward and reverse reactions, and this would indeed be an unusual circumstance.

A change in pressure (either increase or decrease) would have no effect upon either the composition of this equilibrium mixture or the numerical value of the equilibrium constant. Two volumes of gaseous reactants (H_2 and I_2) react to form two volumes of a gaseous product (HI). Because there is no difference in volume, there can be no effect in the sense of Le Châtelier's law and hence no change in the composition of the equilibrium mixture. By the same token, the change in pressure changes the concentration of all components of the equilibrium mixture in the same manner and the numerical value of K must therefore remain the same.

If, at constant temperature, the $[H_2]$ is increased, it follows that the increased probability of collision of H_2 and I_2 molecules is a condition favorable to the formation of HI; consequently the resulting equilibrium mixture is relatively richer in HI molecules and poorer in I_2 molecules. As a result of the initial change in the concentration of hydrogen, the relative concentrations of the components of the equilibrium mixture are readjusted so that there is no change in the numerical value of K.

The same ideas apply to equilibria involving gases where there is a change in volume. In the equilibrium involved in the synthesis of ammonia, for example, an increase in the concentration of hydrogen at constant temperature changes the composition of the equilibrium mixture but does not change the value of K. The net effect is a readjustment in the relative concentrations so that the numerical value of K is

maintained. This of course requires an increase in the concentration of NH_3 and a decrease in the concentration of N_2.

13.10. Calculations Involving Equilibrium Constants

In terms of an entirely general case, assume that 1 mole of a reactant A and 1 mole of a reactant B are brought together in a known volume at some definite temperature and that they react to form products C and D, thus,

$$A + B \rightleftharpoons C + D$$

The problem is to calculate the equilibrium constant for this reaction, and in order to do so it is necessary to know the concentrations of A, B, C, and D that are present when equilibrium becomes established.

If, at equilibrium, it is found that the concentration of product D is 0.3 mole per liter, it is apparent from the foregoing equation that $[C] = [D] = 0.3$. Since A and B react in a 1:1 mole ratio and since each was present initially at a concentration of 1 mole per liter, then the equilibrium concentrations must be $[A] = [B] = 1 - 0.3 = 0.7$ mole per liter. The expression for the equilibrium constant for the reaction is

$$K = \frac{[C] \times [D]}{[A] \times [B]}$$

and by substituting the appropriate molecular concentrations,

$$K = \frac{0.3 \times 0.3}{0.7 \times 0.7}$$

and solving, one finds that

$$K = 0.18$$

Since this value for K is specific for one particular temperature, change in the concentration of one or more of the components of the reaction mixture at this temperature results only in a readjustment of relative concentrations. Whatever the change may be, the result must be such that the numerical value of K remains unchanged. Suppose, for example, that a change is made and that in the newly established equilibrium mixture the molecular concentrations are as follows: $[A] = 0.4$, $[B] = 0.4$, and $[C] = 0.08$ mole per liter. From these values together with the above value for the equilibrium constant, the molecular concentration of D present at equilibrium may be calculated as follows:

$$\frac{0.08 \times [D]}{0.4 \times 0.4} = 0.18$$

$$[D] = 0.36 \text{ mole per liter}$$

Another type of reaction commonly encountered in the study of equilibria involving gases is that in which a relatively complex molecule subdivides (dissociates) into simpler molecules when subjected to elevated temperatures. Thus, N_2O_4 molecules dissociate into, and exist in equilibrium with, NO_2 molecules; the concentrations present at equilibrium depend upon the temperature to which the N_2O_4 is heated. Suppose, for example, that the temperature is such that the N_2O_4 is 75 per cent dissociated and that it is required to find the equilibrium constant.

$$N_2O_{4(gas)} \rightleftharpoons 2NO_{2(gas)}$$

It is seen that complete dissociation of 1 mole (or 1 volume) of N_2O_4 produces 2 moles (or 2 volumes) of NO_2. If one starts with 1 mole (1 volume) of N_2O_4, at equilibrium there is present $1 - 0.75 = 0.25$ mole of N_2O_4. Accordingly, the number of moles of NO_2 present must be $2 \times 0.75 = 1.5$, and the total number of moles of gas present is $0.25 + 1.5 = 1.75$. Since one is concerned with the relative number of moles of each gas present at equilibrium,

$$K = \frac{(\text{moles } NO_2/\text{total moles})^2}{(\text{moles } N_2O_4/\text{total moles})}$$

$$= \frac{(1.5/1.75)^2}{(0.25/1.75)}$$

$$= 5.1$$

In this instance there is only one reactant and one product. Consequently, if at the same temperature the concentration of either were supplemented, the concentration of the other would decrease sufficiently to maintain the above value for the equilibrium constant.

GENERAL EXERCISES

1. What is the difference between physical and chemical equilibria?
2. What advantage is involved in expressing concentration in terms of molecular concentration?
3. State the following laws: (*a*) Le Châtelier's law, (*b*) the law of mass action (see Secs. 13.6 and 13.8 and formulate a *complete* statement of this law).
4. Indicate clearly the nature of the influence of changes in temperature and pressure upon reactions in equilibrium and give one example to illustrate each case.
5. Using the method outlined in Sec. 13.8, derive the expression for the equilib-

rium constant for each of the following equilibria: (*a*) $2SO_{2(gas)} + O_{2(gas)} \rightleftharpoons 2SO_{3(gas)}$, (*b*) $NH_{3(gas)} + HCl_{(gas)} \rightleftharpoons NH_4Cl_{(solid)}$.

6. For each of the following equilibria, write the final expression for the equilibrium constant: (*a*) $2NO_{2(gas)} \rightleftharpoons N_2O_{4(gas)}$, (*b*) $CaCO_{3(solid)} \rightleftharpoons CaO_{(solid)} + CO_{2(gas)}$, (*c*) $CO_{2(gas)} + C_{(solid)} \rightleftharpoons 2CO_{(gas)}$.

7. How is each of the equilibria listed in Exercises 5 and 6 influenced by an increase in pressure?

8. In any given case, what determines the extent to which the forward reaction proceeds toward completion before equilibrium becomes established?

9. Why must it be true that the numerical value of the equilibrium constant changes only with change in temperature?

PROBLEMS

1. For each of the following cases, calculate the molecular concentration in terms of moles per liter:

(*a*) 89.69 g. of sulfur dioxide (SO_2) gas in a volume of 1 liter.

(*b*) 0.0862 g. of carbon monoxide (CO) gas in a volume of 1.36 cc.

(*c*) 19.92 g. of methane (CH_4) gas in a volume of 6.19 liters.

2. For the reaction $A + 2B \rightleftharpoons C + 2D$, calculate the equilibrium constant corresponding to the following equilibrium concentrations: $[A] = 0.5$ mole, $[B] = 0.2$ mole, $[C] = 0.3$ mole, $[D] = 0.5$ mole.

3. If, at the same temperature, the concentration of one of the reactants in the equilibrium in Prob. 2 is changed so that in the new equilibrium mixture, $[A] = 0.8$. $[B] = 0.1$, and $[C] = 0.5$, what is the equilibrium concentration of D?

4. For the equilibrium $2A + 3B \rightleftharpoons 2C + D$, calculate K if 1 liter of the equilibrium mixture contains $\frac{1}{2}$ mole each of A and B, $\frac{1}{4}$ mole of C, and $\frac{3}{4}$ mole of D.

5. If, in the preceding case, a change is made such that in the new equilibrium mixture (at the same temperature) the concentration of A is doubled and the concentrations of B and C remain the same, what is the concentration of D?

6. Ethyl alcohol and acetic acid (1 mole each) react to form 1 mole of water and 1 mole of a compound known as an ester, *i.e.*,

$$\underset{(1\text{ mole})}{\text{Alcohol}} + \underset{(1\text{ mole})}{\text{acid}} \rightleftharpoons \underset{(1\text{ mole})}{\text{water}} + \underset{(1\text{ mole})}{\text{ester}}$$

If, at a given temperature, 1 liter of the equilibrium mixture contains 0.7 mole each of water and ester, what is the equilibrium constant?

7. The formation of gaseous hydrogen iodide from hydrogen gas and iodine occurs in accordance with the equation: $H_2 + I_2 \rightleftharpoons 2HI$. In an experiment conducted at a temperature such that all of the elemental iodine is present as a gas, 24 g. of iodine and 0.5 g. of hydrogen are heated until equilibrium is established. If the equilibrium mixture is found to contain 0.8 g. of iodine in a total volume of 1 liter, (*a*) how many moles of each gas are present in the equilibrium mixture, (*b*) what is the numerical value of the equilibrium constant?

8. If K for an equilibrium mixture of sulfur dioxide, oxygen, and sulfur trioxide at a certain temperature is 0.76, what is the concentration of sulfur trioxide if 1 liter of the mixture contains 0.6 mole each of the other two gases?

SUGGESTED READING

Journal of Chemical Education

FROST, Effect of Concentration on Reaction Rate and Equilibrium, **18**, 272 (1941).

GERMANN, Active and Passive Molecules and the Nature of the Mass Action Equilibrium Constant, **11**, 328 (1934).

HACKERMAN, The Equilibrium Concept in Beginning College Chemistry Courses, **23**, 45 (1946).

CHAPTER 14

IONIZATION

In connection with the study of solutions (Chap. 11) some attention was devoted to the regularities in the manner in which certain physical properties of pure solvents are altered by the presence of solutes. It should be recalled, however, that this study excluded acids, bases, and salts and was restricted to solutes such as sugar and glycerol. This exclusion of certain types of solutes rather obviously suggests that their behavior must be somewhat irregular, or at least different in some respects. A limited knowledge of the various modes of compound formation (Sec. 4.7) having been acquired, it now becomes of interest to see whether the behavior of various solutes can be correlated with their classification in terms of ionic, covalent, and intermediate types. The accomplishment of this objective requires some additional information concerning the ability of substances to act as conductors (carriers) of electricity.

14.1. Conductors of Electricity

It is a familiar fact that metals such as copper, iron, silver, and zinc may be used as conductors of electricity without bringing about any change in the composition of these metals. If the properties of a copper wire are carefully examined before and after its use as a conductor, no detectable difference is found. Metals in general, some nonmetals, and a few other substances possess the property of conduction of electricity without change in chemical composition and are known as *conductors of the first class.* The passage of electricity through a conductor of this type may be looked upon as consisting of a flow of electrons through the shells of the atoms involved. Although the chemist frequently makes use of conductors of the first class, any detailed study of such conductors and conduction processes is perhaps more properly made in connection with courses in physics and electrical engineering.

Of greater interest to the chemist are those conductors which consist of solutions and which are known as *conductors of the second class.* These are characterized by the fact that, when they are used as carriers of electricity, changes in chemical composition always occur. Further-

more, the process by which solutions conduct electrical currents may not be likened to the "flow of electrons" suggested above, and it therefore becomes necessary to learn more about the state in which solutes exist in solutions before the distinction can be clarified.

14.2. Conduction by Solutions

If one should prepare aqueous solutions (all 0.1 *M*) of a wide variety of compounds and test the ability of these solutions to act as conductors of electricity, it would be found possible to classify all of these solutions roughly into three classes: (*a*) nonconducting solutions, (*b*) weakly conducting solutions, and (*c*) strongly conducting solutions. Since the pure solvent (water) is only an exceedingly poor conductor and many pure solutes are nonconductors of electric currents, the property of conducting electricity must be peculiar to the solutions.

Since the following discussions are to be concerned with conducting solutions, those substances whose solutions are nonconductors need not be made the object of any extensive discussion. **Those substances whose solutions do not conduct electricity are known as nonelectrolytes.** Substances of this type are either entirely covalent or at least predominantly covalent in character and are illustrated by such compounds as alcohol, glycerol, and sugar. It may not be concluded, however, that all covalent compounds are nonelectrolytes.

Electrolytes. Those substances whose solutions are conductors of electricity are called electrolytes. Depending upon the *extent* to which their solutions act as conductors, this class of solutes may be subdivided into two groups which are known as *weak electrolytes* and *strong electrolytes*. For the purposes of the immediate discussion, acetic acid is used as an example of a typical weak electrolyte and sodium chloride is considered as representative of strong electrolytes.

If one should measure the electrical conductivity of a 1 *M* solution of $HC_2H_3O_2$ in water (*i.e.*, the extent to which the solution is capable of conducting electricity), the solution would be found to be a rather poor conductor, and the magnitude of the current carried by the solution could, by means of suitable electrical instruments, be measured in amperes. Now if this same solution is diluted until it is 0.5 *M* with respect to $HC_2H_3O_2$, this more dilute solution will be found to be a better conductor (in relation to the total quantity of solute present) than the original 1 *M* solution. Progressive dilution to 0.1 *M*, 0.01 *M*, 0.001 *M*, etc., together with corresponding conductivity measurements

shows that, with increasing dilution, the conductivity increases until an apparent maximum is reached. Thereafter, further dilution does not result in any appreciable increase in conductivity. The results of this experiment may be represented graphically by plotting conductance against dilution as shown in Fig. 69*a*.

A similar experiment using the strong electrolyte Na^+Cl^- as the solute would be found to lead to similar results. Of course, the conductivity is found to be different from that of an acetic acid solution of the same concentration, but the conductivity is found to increase with increasing dilution in much the same manner as described above. This

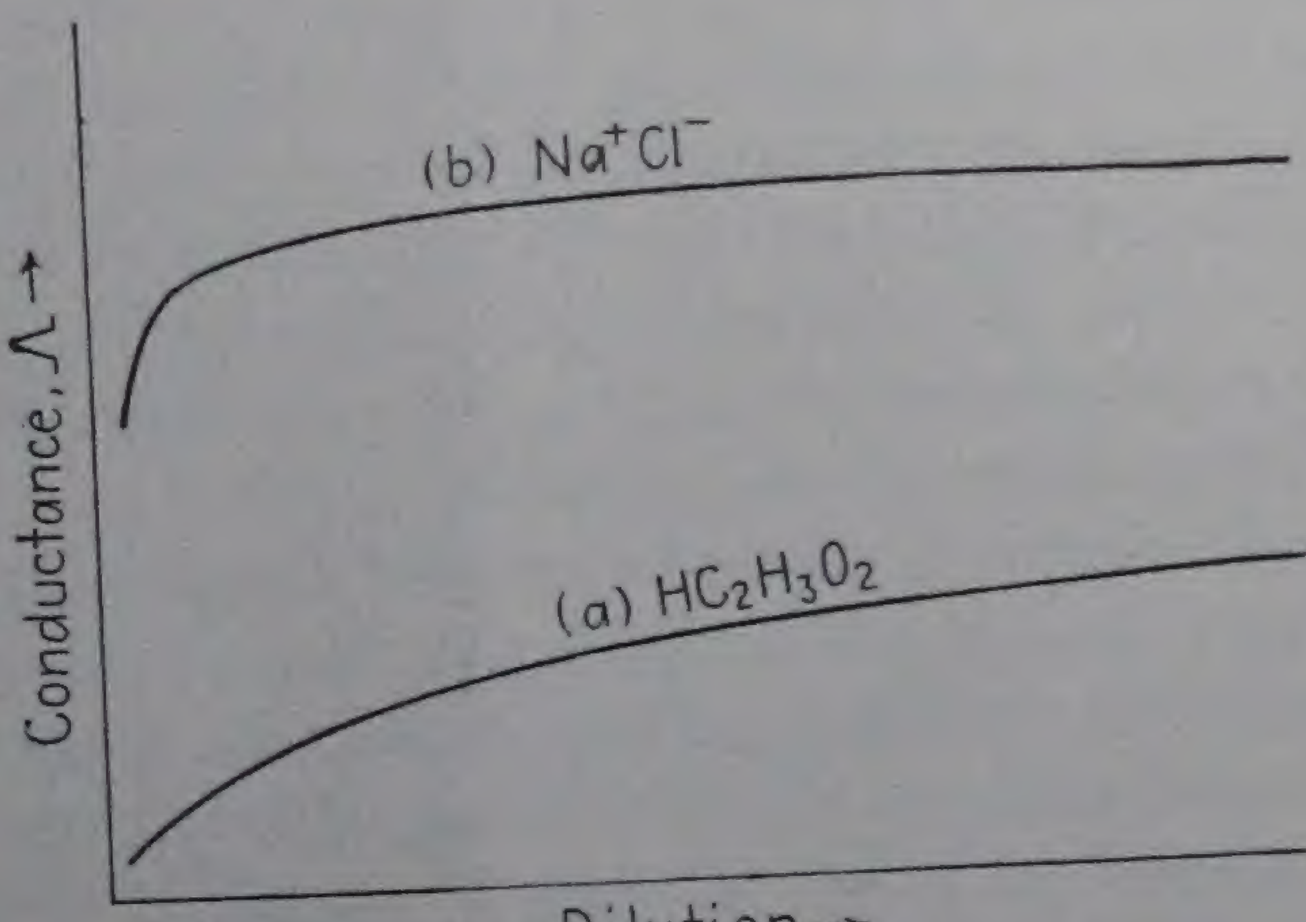

FIG. 69. Variation in the conductance of a weak and a strong electrolyte with dilution.

similarity is made evident by a comparison of Fig. 69*b* with Fig. 69*a*. The results of these two experiments would seem to require explanations to account for the fact that these solutions are conductors and for the fact that conductivity increases with dilution until a maximum conductivity is realized.

14.3. Theory of Arrhenius

In the year 1887, the Swedish chemist Svante Arrhenius (Fig. 70), enunciated a theory designed to explain the state in which electrolytes exist in solutions. This theory holds that whenever an acid, a base, or a salt is dissolved in a solvent such as water, the solute *then* subdivides into smaller units which bear electrical charges. The ability of a solution of an electrolyte to act as a conductor of electricity was attributed to the presence of these charged particles, which Arrhenius called *ions* (Sec. 4.8), and to the ability of those ions to move through the solution. Also in terms of the theory of Arrhenius, the actual

charge (either positive or negative) on a particular ion was believed to be equal to the valence of the atom or radical involved. Another noteworthy feature of the theory also lay in the fact that Arrhenius believed that ionization was incomplete except in extremely dilute solutions and that the actual extent to which the molecules of the solute separate into ions is dependent upon concentration.

According to the views of Arrhenius, the ionization of sodium chloride and acetic acid may be represented as follows:

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$HC_2H_3O_2 \rightleftharpoons H^+ + (C_2H_3O_2)^-$$

Similarly, the ionization of other electrolytes would be represented by the equilibria,

$$Zn(NO_3)_2 \rightleftharpoons Zn^{++} + 2(NO_3)^-$$

$$CuSO_4 \rightleftharpoons Cu^{++} + (SO_4)^=$$

$$BiCl_3 \rightleftharpoons Bi^{+++} + 3Cl^-$$

$$NH_4OH \rightleftharpoons (NH_4)^+ + (OH)^-$$

$$Fe_2(SO_4)_3 \rightleftharpoons 2Fe^{+++} + 3(SO_4)^=$$

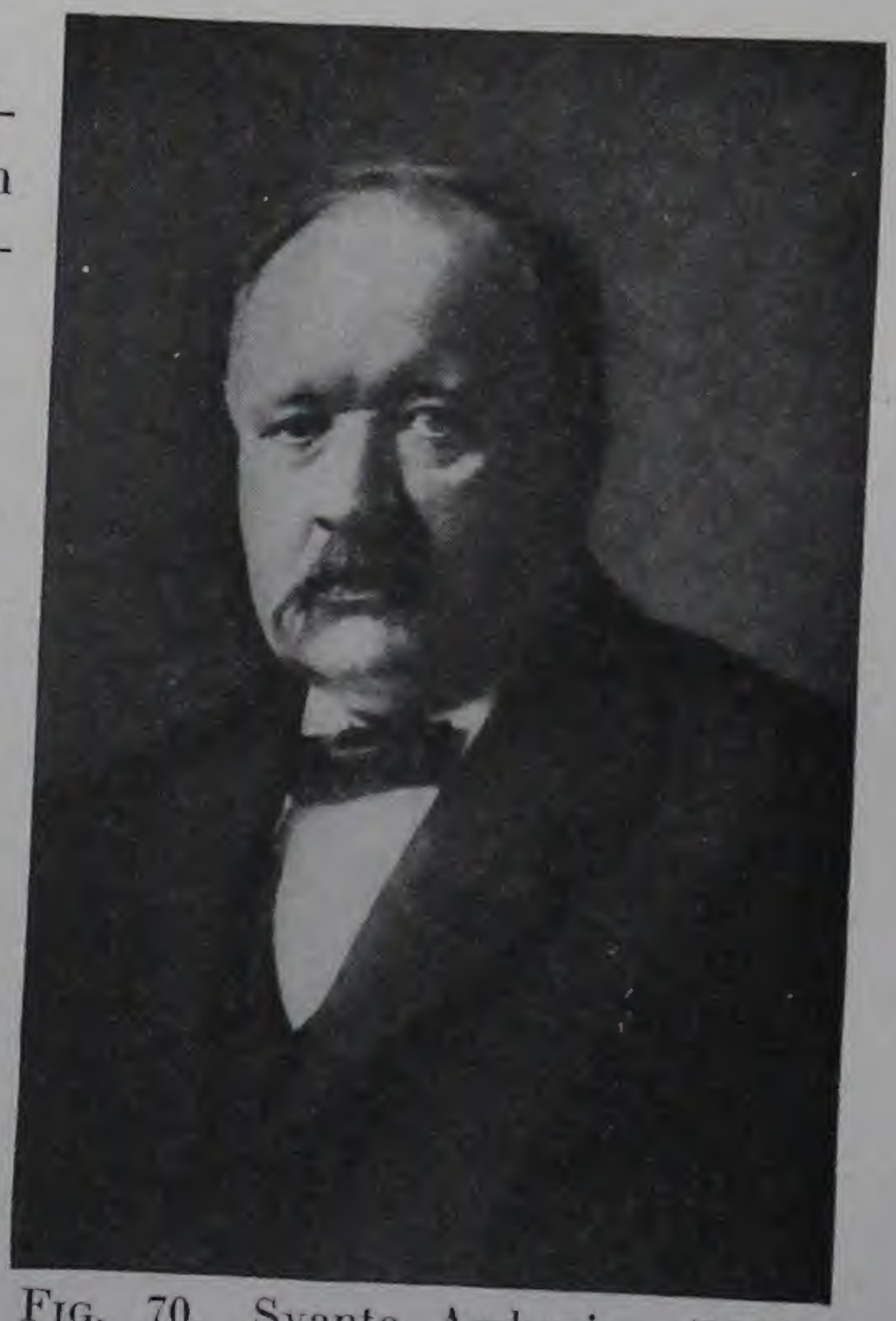

FIG. 70. Svante Arrhenius (1859–1927). (*Courtesy of The Edgar Fahs Smith Memorial Collection in the History of Chemistry, The University of Pennsylvania.*)

In the light of the theory of Arrhenius, it becomes possible to explain why the conductivity of a solution of an electrolyte increases with dilution and reaches a maximum value. In the case of acetic acid, for example, the ionization in increasingly dilute solutions results in increasing numbers of ions in the equilibrium mixture. Accordingly, a concentrated solution would be expected to be a poor conductor because most of the $HC_2H_3O_2$ would be present as molecules and there would be relatively few ions present in the solution. As this solution is made progressively more dilute, more molecules would ionize, the solution would become richer in ions and hence a better conductor. The recombination of H^+ and $(C_2H_3O_2)^-$ ions to form un-ionized molecules is, under these conditions, rendered less probable owing to the fact that in the dilute solution the ions are separated through greater distances. Finally, if the solution is made extremely (infinitely)

dilute, all the molecules should separate into ions; the solution should then exhibit its maximum conductivity, and further dilution should produce no further increase in conductivity. This interpretation is consistent with the experimental results described above and shown graphically in Fig. 69. Although the theory of Arrhenius has been modified extensively since its inception, it is still useful in explaining the behavior of the great majority of the covalent compounds that behave as weak electrolytes.

In recent times, however, the Arrhenius theory has been shown to be inadequate so far as strong electrolytes (ionic compounds) and some weak electrolytes are concerned. This failure of the theory of Arrhenius may be illustrated by the case of sodium chloride. It should be recalled that sodium ions and chloride ions are formed when the ionic compound sodium chloride is formed by the process of loss and gain of electrons,

$$Na^0 + Cl^0 \rightarrow Na^+Cl^-$$

This fact has been confirmed by the examination of Na^+Cl^- crystals by means of X rays. Such studies have shown that, in the crystal, each ion occupies a fixed position in space and is surrounded by ions of opposite charge. Consequently, any given sodium ion cannot be said actually to be united with any one particular chloride ion, and this fact leads to the conclusion that discrete *molecules* of sodium chloride do not exist as such. Solid sodium chloride (and other ionic compounds as well) is to be looked upon as an electrically neutral body consisting of positive and negative ions and not involving the existence of actual unit molecules except in the sense that the crystal as a whole may be thought of as a "giant molecule."

Since ionic compounds consist of ions by virtue of their mode of formation and since the theory of Arrhenius holds that ions are formed only when the electrolyte is dissolved in a suitable solvent, some other explanation must be offered for the behavior of a strong electrolyte such as sodium chloride.

14.4. Theory of Debye and Hückel

If, in a concentrated solution, a strong electrolyte is present entirely in the form of ions, one might anticipate that such a solution would at once exhibit its maximum conductivity and that its conductivity would not be increased by dilution. That such is not the case has already been indicated (Sec. 14.2). A plausible explanation of behavior of this sort was provided by the theory of Debye and Hückel. In its

most elementary aspects, this theory holds that, in a concentrated solution of a strong electrolyte, the condition of each ion is much like that which exists in the crystal. That is, each positive ion is surrounded by an "atmosphere" of negative ions (and vice versa) so that any given ion is attracted by oppositely charged ions (owing to electrostatic attraction) and is therefore retarded in its motion through the solution. This amounts to saying that, although the solute is present at a given concentration entirely in the form of ions, these ions are not free to move about in the solutions because of the hindering attraction of ions of the opposite charge. Consequently, the *apparent concentration* (or effective concentration) of the ions is different from the actual concentration at which the solute is present in the solution. Thus, ions may be present in the solution without being entirely *active* as individual ions; the solute may be completely ionized, but the ions are not completely disassociated from the influence of one another. One should not, however, adopt the view that some ions are completely free or active while others are completely inactive. More properly, each ion should be thought of as exhibiting a certain degree of activity.

Because the effective concentration of ions in solutions of strong electrolytes differs from the concentration of the corresponding solutes in these solutions, it is necessary for many purposes to multiply the concentration by a correction factor called the *activity coefficient*, f (see Table 18). The numerical values for the activity coefficients for different electrolytes must be determined by experiment, and they vary with change in both temperature and concentration. As applied to strong electrolytes, the term activity therefore amounts to a corrected concentration.

In terms of the interionic attraction theory of Debye and Hückel, the conductivity of solutions of strong electrolytes may be understood. The concentrated solution is not so good a conductor because the ions are so close together that they are unable to move as readily through the solution; *i.e.*, they are greatly restricted owing to the proximity of oppositely charged ions. However, as the solution is progressively diluted, the ions become separated through greater distances, their mobility is increased, and they are able to exhibit a greater degree of unhindered activity; hence, the conductivity increases. Finally, if the solution is made sufficiently (infinitely) dilute, the ions are so far apart that they are relatively unaffected by the other ions and are able to exhibit essentially 100 per cent activity. Under these conditions, of course, the solution exhibits the maximum conductivity possible in relation to the number of ions in the solution.

On the assumption that the theory of Debye and Hückel provides a fairly accurate picture of the condition in which strong electrolytes exist in solution, the ionization scheme

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

proposed by Arrhenius for strong electrolytes such as sodium chloride is entirely inappropriate.

A Comparison of the Two Theories. In the last analysis, there is no great difference between the theory of Arrhenius and that of Debye and Hückel. The former (1) emphasizes the formation of ions from un-ionized molecules in the solution, (2) is concerned primarily with the number of ions produced at any given concentration, and (3) is useful in explaining the behavior of most weak electrolytes. On the other hand, the interionic-attraction theory (1) emphasizes both the number of and the charge on the ions, (2) is concerned largely with the activity of the ions present at any particular concentration, and (3) is useful in interpreting the behavior of strong electrolytes and also those covalent compounds which behave as strong electrolytes when they are dissolved in solvents such as water. Finally, it should be pointed out that the interionic-attraction theory is applicable also to that portion of a weak electrolyte which is ionized in solution.

14.5. Influence of Electrolytes upon the Physical Properties of Pure Solvents

It has already been pointed out (Chap. 11) that the vapor pressure, boiling temperature, and freezing temperature of a pure solvent, such as water, are changed in a *regular* fashion by the presence of nonelectrolytes such as sugar and glycerol. Electrolytes, on the other hand, produce effects that are irregular in the sense that the effects produced are in the same direction but are *excessive*. Thus, a 1 *m* solution of sodium chloride actually freezes at $-3.30°$C. and not at $-1.86°$ as would be the case for a 1 *m* solution of sugar. The regular lowering of the freezing temperature to the extent of 1.86° is characteristic of solutions of nonelectrolytes and is attributed to the presence of 6.02×10^{23} *molecules* (particles) of the solute. In the case of sodium chloride, however, the solute is present not as molecules but rather as ions which are active to only a limited degree at a concentration as high as 1 *m*. If the ions of sodium chloride were completely active in a 1 *m* solution, the number of particles (ions) would be $2 \times (6.02 \times 10^{23})$ and the freezing temperature would be $-3.72°$ ($2 \times 1.86°$). The fact that the lowering is 3.30° and not 3.72° may be taken as indication of

the degree of activity of the sodium and chloride ions in a 1 *m* solution of sodium chloride.

Similar excessive effects are produced by electrolytes upon the boiling temperatures of pure solvents, and for the same reasons. For example, the boiling temperature of a 1 *m* solution of the weak electrolyte $HC_2H_3O_2$ is 100.522° and not 100.515° as in the case of a nonelectrolyte. The elevation of the boiling temperature is a little greater than 0.515 for the reason that a few of the original 6.02×10^{23} molecules have ionized to form H^+ and $(C_2H_3O_2)^-$ ions, thus providing a total number of particles greater than 6.02×10^{23}.

Determination of Degree of Ionization. The extent to which a weak electrolyte at known concentration affects the boiling temperature, freezing temperature, etc., of a pure solvent may be used to determine degree of ionization. For example, the 1 *m* solution of the weak electrolyte $HC_2H_3O_2$ exhibited a boiling temperature of 0.522, or 0.007° greater than the 0.515° elevation produced by an equivalent concentration of a nonelectrolyte. Accordingly the degree of ionization (expressed in per cent) is

$$\frac{0.007}{0.515} \times 100 = 1.3 \text{ per cent}$$

This in turn means that 1.3 per cent of the original 6.02×10^{23} molecules of $HC_2H_3O_2$ ionized to form H^+ and $(C_2H_3O_2)^-$.

14.6. Weak Electrolytes

In connection with much of the subject matter that is to follow, it is necessary for the student to acquire information concerning those common acids, bases, and salts which behave as weak electrolytes.

Acids. The common acids that behave as weak electrolytes are listed in Table 16. For those acids which contain more than one replaceable hydrogen, it is necessary to inquire as to the manner in which such acids ionize. The ionization of an acid such as carbonic acid occurs in two stages or "steps," thus,

$$H_2CO_3 \rightleftharpoons H^+ + (HCO_3)^- \tag{1}$$

to form first a hydrogen ion and a hydrogen carbonate ion, $(HCO_3)^-$, which then participates in the second step of the ionization process,

$$(HCO_3)^- \rightleftharpoons H^+ + CO_3^{=} \tag{2}$$

Similarly, the ionization of H_3PO_4 is a three-stage process involving

the equilibria,

$$H_3PO_4 \rightleftharpoons H^+ + (H_2PO_4)^- \quad (1)$$

$$(H_2PO_4)^- \rightleftharpoons H^+ + (HPO_4)^= \quad (2)$$

$$(HPO_4)^= \rightleftharpoons H^+ + (PO_4)^{\equiv} \quad (3)$$

Many acids that ionize in this manner are fairly strong electrolytes with respect to the first step in the ionization process, but the secondary and any subsequent steps are characteristic of weak electrolytes. Thus in the above case, the second step cannot occur extensively since it is limited by the extent to which $(H_2PO_4)^-$ ions are available.

TABLE 16

DEGREE OF IONIZATION OF SOME WEAK ELECTROLYTES (ACIDS) IN 0.1 NORMAL SOLUTIONS AT 25°C.

Acid	Ionization process	Degree of ionization, %
Acetic	$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$	1.3
Hydrocyanic	$HCN \rightleftharpoons H^+ + CN^-$	0.002
Hydrosulfuric	$H_2S \rightleftharpoons H^+ + HS^-$	0.07
Hydrosulfide ion	$HS^- \rightleftharpoons H^+ + S^=$	$0.0_{13}12$
Carbonic	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	0.17
Hydrogen carbonate ion	$HCO_3^- \rightleftharpoons H^+ + CO_3^=$	0.01
Sulfurous	$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$	34.0
Hydrogen sulfite ion	$HSO_3^- \rightleftharpoons H^+ + SO_3^=$	0.1
Phosphoric	$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	27.0
Dihydrogen phosphate ion	$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^=$	0.14
Hydrogen phosphate ion	$HPO_4^= \rightleftharpoons H^+ + PO_4^{\equiv}$	0.0002

Since only a few of the $(H_2PO_4)^-$ ions undergo further ionization according to step (2), the third stage can be realized to only an exceedingly small extent.

Bases. The only common soluble base that acts as a weak electrolyte is ammonium hydroxide, which is formed by the reaction between gaseous ammonia and water,

$$NH_3 + H_2O \rightleftharpoons NH_4OH$$

and which ionizes according to the equilibrium,

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

In 0.1 *N* solution at 25°, NH_4OH is ionized to the extent of only 1.3 per cent.

Salts. Although most salts are strong electrolytes, there are a few common ones whose behavior is more nearly typical of weak electrolytes. These rather exceptional cases are listed in Table 17.

TABLE 17

WEAK ELECTROLYTES (SALTS)

Name	Formula
Lead acetate	$Pb(C_2H_3O_2)_2$
Ferric thiocyanate	$Fe(SCN)_3$
Mercuric thiocyanate	$Hg(SCN)_2$
Mercuric chloride	$HgCl_2$
Mercuric cyanide	$Hg(CN)_2$
Cadmium chloride	$CdCl_2$
Cadmium bromide	$CdBr_2$
Cadmium iodide	CdI_2

Water. A very important weak electrolyte is water itself. Water molecules ionize to only an extremely slight extent under ordinary conditions. An idea as to the very small number of ions in pure water may be gained from the fact that the total weight of OH^- in 1 ton of water is 0.0017 g. More accurately, the concentration of H^+ (and also OH^-) in pure water is 1×10^{-7} N (*i.e.*, one ten-millionth normal).

14.7. Strong Electrolytes

For the purposes of the work that is to follow, all electrolytes that have not been designated as "weak" in the preceding section are to be considered as strong electrolytes. As is shown later (Sec. 14.8), this viewpoint is neither entirely accurate nor justifiable except on the basis of convenience.

It is not practical here to list any great number of strong electrolytes. However, a brief list is given in Table 18, together with the activity coefficients, and a classification of the examples cited on the basis of the valence of the ions involved.

By inspection of the data of Table 18 it is seen that there is a definite relationship between the activity and the charge type of the ions. This is wholly in accord with the ideas embodied in the theory of Debye and Hückel. It should be rather obvious that an ion bearing two units of positive charge should be more effective in hindering the movement of a negative ion than an ion bearing only one positive charge. Similarly the $SO_4^=$ should exert a greater force of attraction toward a Na^+, for example, than would a Cl^-. It is therefore a fairly safe generalization to state that, *at equivalent concentrations, the activity decreases with increase in the magnitude of the ionic charges.*

TABLE 18

ACTIVITY COEFFICIENTS OF SOME TYPICAL STRONG ELECTROLYTES IN 0.1 MOLAL SOLUTIONS AT 25°C.

Electrolyte	Activity coefficient f	Classification
Acids:		
H^+Br^-	0.802	Uni-univalent
H^+Cl^-	0.796	
$H^+(NO_3)^-$	0.790	
$H_2^+(SO_4)^=$	0.313	Uni-bivalent
Bases:		
$K^+(OH)^-$	0.772	Uni-univalent
$Na^+(OH)^-$	0.765	
$Li^+(OH)^-$	0.742	
$Ba^{++}(OH)_2^-$	.....	Bi-univalent
Salts:		
Li^+Br^-	0.794	Uni-univalent
Na^+I^-	0.788	
Na^+Cl^-	0.778	
K^+Br^-	0.765	
K^+Cl^-	0.764	
$K^+(NO_3)^-$	0.732	
$Ag^+(NO_3)^-$	0.723	
$Ca^{++}Cl_2^-$	0.528	Bi-univalent and uni-bivalent
$Ba^{++}Cl_2^-$	0.495	
$Na_2^+(SO_4)^=$	0.435	
$K_2^+(SO_4)^=$	0.420	
$Mg^{++}(SO_4)^=$	0.166	Bi-bivalent
$Cd^{++}(SO_4)^=$	0.160	
$Cu^{++}(SO_4)^=$	0.158	

14.8. Intermediate Types

It is essential at this juncture to call attention to the fact that the foregoing classification of electrolytes into two broad classes should not be accepted without reservations. The student should keep in mind that weak electrolytes are predominantly covalent and that strong electrolytes are (with but relatively few exceptions) predominantly ionic. But, just as there are all possible gradations between covalent and ionic compounds (Sec. 4.10), so there must be a correspondingly large number of electrolytes that are intermediate between the very weak and the very strong electrolytes. In this and in other similar situations, there is some considerable merit in the practice of emphasiz-

ing the extreme types of behavior in the beginning course and deferring to the more advanced courses the study of the generally more complicated behavior of intermediate types.

14.9. Acid Salts

Since the ionization of acids containing two or more replaceable hydrogen ions occurs in stages or steps (Sec. 14.6) and since the extent of each stage of ionization is greater than that of any subsequent step, the neutralization of such acids should also be expected to occur in a stepwise fashion. Consider, for example, the first step in the ionization of sulfurous acid,

$$H_2SO_3 \rightleftharpoons H^+ + (HSO_3)^-$$

Owing to the fact that this stage of ionization is so much more extensive than the subsequent ionization of the hydrogen sulfite ion,

$$(HSO_3)^- \rightleftharpoons H^+ + (SO_3)^=$$

it might be anticipated that the neutralization of sulfurous acid by a base such as sodium hydroxide would occur as follows:

$$H_2SO_3 + Na^+(OH)^- \rightarrow H_2O + Na^+(HSO_3)^-$$

The strong electrolyte $Na^+(HSO_3)^-$, however, consists of an anion, $(HSO_3)^-$, which is a weak electrolyte but which is capable of further ionization.

$$(HSO_3)^- \rightleftharpoons H^+ + (SO_3)^=$$

Consequently a further reaction with a base is possible, thus,

$$Na^+(HSO_3)^- + Na^+(OH)^- \rightarrow H_2O + Na_2^+(SO_3)^=$$

The neutralization of acids containing two or more replaceable hydrogen atoms does occur in this stepwise fashion, and, in the laboratory, one may neutralize such an acid either completely or partly, depending upon the quantity of base employed. The stepwise neutralization of arsenic acid serves as a further example,

$$H_3AsO_4 + K^+(OH)^- \rightarrow H_2O + K^+(H_2AsO_4)^-$$
$$K^+(H_2AsO_4)^- + K^+(OH)^- \rightarrow H_2O + K_2^+(HAsO_4)^=$$
$$K_2^+(HAsO_4)^= + K^+(OH)^- \rightarrow H_2O + K_3^+(AsO_4)^{\equiv}$$

If a base containing more than one $(OH)^-$ is used, a similar result is obtained.

$$2H_2CO_3 + Ba^{++}(OH)_2^- \rightarrow 2H_2O + Ba^{++}(HCO_3)_2^-$$
$$Ba^{++}(HCO_3)_2^- + Ba^{++}(OH)_2^- \rightarrow 2H_2O + 2Ba^{++}(CO_3)^=$$

The preceding examples have pointed to the existence of the compounds $Na^+(HSO_4)^-$, $K^+(H_2AsO_4)^-$, $K_2^+(HAsO_4)^=$, and $Ba^{++}(HCO_3)_2^-$. Like acids, all these compounds contain replaceable hydrogen and at the same time appear to be salts, since they arise from reactions of neutralization. Compounds of this type are known as *acid salts*. These acid salts are named in different ways, two of which are illustrated in Table 19.

TABLE 19

NOMENCLATURE OF ACID SALTS

Formula	Preferred name	Alternative name
$Na^+(HSO_3)^-$	Sodium hydrogen sulfite	Sodium acid sulfite
$K^+(H_2AsO_4)^-$	Potassium dihydrogen arsenate	Primary potassium arsenate
$K_2^+(HAsO_4)^=$	Dipotassium hydrogen arsenate	Secondary potassium arsenate
$Ba^{++}(HCO_3)_2^-$	Barium hydrogen carbonate	Barium acid carbonate
$Na^+(HCO_3)^-$	Sodium hydrogen carbonate*	Sodium acid carbonate

* The common name for this compound is "sodium bicarbonate." However, in systematic nomenclature the prefix *bi-* should be avoided in naming acid salts.

By analogy to acid salts, the existence of *basic salts* would certainly appear as a logical possibility. Many salts of this type are indeed well known, but a consideration of their mode of formation and properties is deferred to a later section. Salts such as $Na_2^+(SO_3)^=$, $K_3^+(AsO_4)^{\equiv}$, and $Ba^{++}(CO_3)^=$, which represent the products obtained by complete neutralization, are called *normal salts*, and these are assigned names in accordance with the rules of nomenclature previously discussed.

14.10. Amphoteric Bases

In Sec. 12.5 it was pointed out that certain hydroxides may act either as bases or as acids. As such, their characteristic behavior depends upon the fact that they exhibit a low degree of ionization, *i.e.*, they act as either weak acids or weak bases. Accordingly, it is to be expected that the ionization of these substances would occur in a manner analogous to that already indicated for certain weak acids (Secs. 14.6 and 14.9).

If, for example, zinc hydroxide acts as a base, the first step in its ionization process

$$Zn(OH)_2 \rightleftharpoons (ZnOH)^+ + OH^-$$

gives rise to a positive ion which upon reaction with the negative ion of an acid such as hydrochloric,

$$(ZnOH)^+ + OH^- + H^+ + Cl^- \rightarrow H_2O + Zn(OH)Cl$$

leads to the formation of a product which is in part a salt and in part a base since it contains the characteristically basic (OH) group. Thus, Zn(OH)Cl is classed as a basic salt. At least to a slight extent the $(ZnOH)^+$ is capable of a secondary ionization step,

$$(ZnOH)^+ \rightleftharpoons Zn^{++} + OH^-$$

and reaction with a second equivalent of hydrochloric acid would of course lead to the normal salt $ZnCl_2$.

In its role as an acid, H_2ZnO_2 ionizes in the same manner as other weak acids,

$$H_2ZnO_2 \rightleftharpoons H^+ + HZnO_2^-$$

$$HZnO_2^- \rightleftharpoons H^+ + ZnO_2^=$$

and its neutralization by a strong base such as sodium hydroxide occurs in the corresponding stepwise fashion previously illustrated.

14.11. Complex Ions

The kinds of simple positive and negative ions considered thus far do not give an adequate appreciation of the complexity of the ionic species that exist in solvents such as water. In a broad sense, all ions may be (and usually are) classified as either simple or complex, where the former category includes ions such as H^+, NH_4^+, Cu^{++}, Al^{+++}, Cl^-, $SO_4^=$, $C_2H_3O_2^-$, and $PO_4^{\equiv}$. Ions usually classified as complex ions are those formed by the union of simple ions with one or more neutral molecules.

This classification of ions is quite illusory. The ammonium ion, for example, is complex in the sense that it is the product of the combination of a hydrogen ion with a molecule of ammonia,

$$H^+ + NH_3 \rightarrow NH_4^+$$

Similarly, in water solution the hydrogen ion is associated with one or more molecules of the solvent and is commonly represented as $(H \cdot H_2O)^+$ or, more simply, H_3O^+. Thus the proton is *hydrated* in aqueous solution, and this particular species is given the special name *hydronium* ion because of its importance in connection with acidity phenomena (Sec. 15.4). Most other so-called simple ions are hydrated in aqueous solutions, *e.g.*, $[K(H_2O)_4]^+$, $[Al(H_2O)_6]^{+++}$, and even though these may properly be considered to be complex ions, their representation as K^+ and Al^{+++} in the writing of formulas and chemical equations is partly a matter of convenience and partly the result of the fact that it is not

yet possible to determine the exact number of water molecules associated with a particular ion at a given concentration.

More typical examples of species normally thought of as complex ions are those shown enclosed in brackets below.

$$Ag^+ + 2NH_3 \rightarrow [Ag(NH_3)_2]^+$$

$$Co^{+++} + 6NH_3 \rightarrow [Co(NH_3)_6]^{+++}$$

$$CN^- + AgCN \rightarrow [Ag(CN)_2]^-$$

$$2Cl^- + CdCl_2 \rightarrow [CdCl_4]^=$$

Ions of this type have properties that make them useful in accomplishing chemical separations. Numerous such applications are encountered in laboratory work in qualitative chemical analysis.

GENERAL EXERCISES

1. Distinguish clearly between the following: (*a*) conductors of the first class and conductors of the second class, (*b*) electrolytes and nonelectrolytes, (*c*) strong electrolytes and weak electrolytes, (*d*) atoms and ions, (*e*) acid salts and normal salts.

2. In what way are weak electrolytes, strong electrolytes, and intermediate types related to their mode of formation?

3. What facts contributed to the partial failure of the theory of Arrhenius and gave rise to the theory of Debye and Hückel?

4. Give a brief comparison of the theories of Arrhenius and of Debye and Hückel.

5. Write systematic names for the following acid salts: $Na^+(SH)^-$, $Li^+(HSO_4)^-$, $Ca^{++}(H_2PO_4)_2^-$, $K_2^+(HPO_3)^=$.

6. What is the maximum number of acid salts that might be produced from each of the following acids: (*a*) H_2SiO_3, (*b*) H_2ZnO_2, (*c*) HNO_2, (*d*) H_3AlO_3, (*e*) H_4ZrO_4, (*f*) H_2Se, (*g*) $HAsO_3$, (*h*) H_3PO_4?

7. Where such ionization is possible, write equations (equilibria) showing the stepwise ionization of each of the acids listed in Ex. 6.

8. If only about 1 per cent of the NH_4OH molecules in a 1 *m* solution of this base are ionized, how may one account for the fact that *all* of the NH_4OH—not merely the 1 per cent—is neutralized when sufficient hydrochloric acid is added?

9. Suggest ionization schemes for the amphoteric bases $Pb(OH)_2$ and $Al(OH)_3$.

10. Would it be proper to classify water as an amphoteric base? Why?

11. What analogy exists between amphoteric hydroxides and amphoteric elements?

12. If the activity coefficient for a certain strong electrolyte at a given concentration and temperature is 0.65, how will this numerical value change if the solution is diluted at the same temperature? Under what conditions does the numerical value of the activity coefficient become equal to unity?

PROBLEMS

See problems at end of Chap. 15.

SUGGESTED READING

Journal of Chemical Education

JOHNSON, Electricity and Matter, **4,** 1088 (1927).

HUNT and BRISCOE, Factors Determining Electrolytic Dissociation, **6,** 1716 (1929).

HAZELHURST, An Approach to the Theory of Ionization, **14,** 316 (1937).

DAVIDSON, Solutions of Electrolytes, **12,** 24 (1935).

WEST and GAHLER, The Apparent Degree of Ionization of Hydrochloric, Sulfuric, and Acetic Acids, **19,** 366 (1942).

RONNEBERG, Place the Arrhenius Theory in Proper Perspective, **26,** 400 (1949).

HURD, Notes on the Formation and Stability of Complex Ions, **25,** 394 (1948).

CHAPTER 15

ION EQUILIBRIA

On the basis of a knowledge of the general characteristics of reversible reactions and chemical equilibrium (Chap. 13) together with information acquired in the study of theories of ionization (Chap. 14), it is possible to pursue further the study of reactions of ions in solution. The ionization of weak electrolytes and numerous important kinds of metathetical reactions (Chap. 17) are concerned with equilibria involving ions. The study of such equilibria is particularly important in relation to their applications to problems in analytical chemistry, both qualitative and quantitative.

15.1. Ionization of Weak Electrolytes

The ionization of a solution of a weak electrolyte is represented as an equilibrium between un-ionized molecules of the solute and its ions. For example, the following equations illustrate, respectively, the ionization of a weak acid, $HC_2H_3O_2$, and a weak base, NH_4OH:

$$HC_2H_3O_2 \rightleftharpoons H^+ + (C_2H_3O_2)^-$$

$$NH_4OH \rightleftharpoons (NH_4)^+ + (OH)^-$$

In a 0.1 *M* solution of ammonium hydroxide, the concentration of ammonium and hydroxyl ions is very low, since at this concentration NH_4OH is only 1.3 per cent ionized (Sec. 14.6). Because these two ions must be formed in equivalent amounts, the actual concentrations present in a 0.1 *M* solution are

$$[NH_4^+] = [OH^-] = 0.1 \times 0.013 = 0.0013\ M$$

Thus, while the solution is 0.1 *M* with respect to the total potential NH_4OH content of the solution, it is only 0.0013 *M* with respect to NH_4^+ and OH^-, owing to the slight degree of ionization. The equilibrium constant for this reaction is given by the following expression:

$$\frac{[NH_4^+] \times [OH^-]}{[NH_4OH]} = K_i$$

where K_i represeuts an "ionization constant," which is nothing more than the equilibrium constant for an ionization equilibrium. By sub-

stituting the actual numerical values for the three concentration terms,

$$\frac{0.0013 \times 0.0013}{0.1 - 0.0013} = K_i$$

and solving, the numerical value for the ionization constant is obtained:

$$K_i = \frac{(0.0013)^2}{0.0987}$$

$$= 0.0000171$$

$$= 1.71 \times 10^{-5}$$

As is true of any equilibrium constant, the numerical value of K_i changes with change in temperature, but not with change in the concentration of any of the components. In the above case, the concentration of un-ionized molecules of ammonium hydroxide is so large in comparison with the concentration of its ions that, for most purposes, the term [NH_4OH] may be considered to be constant. By incorporating this term in the constant and considering only the concentration of the ammonium and hydroxyl ions, one obtains

$$K_i = [NH_4^+] \times [OH^-]$$

$$= 0.0013 \times 0.0013$$

$$= 1.69 \times 10^{-6}$$

This constant is more properly referred to as the *ion product constant*. The particular numerical value given above is that for a 0.1 M solution of NH_4OH, and different values would be found for different concentrations and, of course, for different temperatures. For such cases, where the concentration of the molecular species is quite variable, the ion product constant must be calculated for each concentration.

Similar calculations may be made for any weak electrolyte. Suppose, for example, that one were interested in using a solution of some weak acid HA (where A is any appropriate negative ion), in which the total acid concentration is 1.0 M and the concentration of hydrogen ions is 1×10^{-5} M. One might need to know the value for the ionization constant and to know what percentage of the acid is ionized; these calculations may be made as follows:

$$HA \rightleftharpoons H^+ + A^-$$

$$K_i = \frac{[H^+] \times [A^-]}{[HA]}$$

For the reason that the ionization of one HA molecule produces one

H^+ and one A^-,

$$[H^+] = [A^-] = 1 \times 10^{-5}\ M$$

Subtraction of the fraction of HA ionized from the quantity initially provided gives the concentration present at equilibrium,

$$1.0\ M - 1 \times 10^{-5}\ M = [HA]$$

but it is evident by inspection that this result is a number only slightly less than 1.0. For most purposes, therefore, it is permissible to consider $[HA] = 1.0\ M$ and thereby simplify the calculations without introducing any really significant error. Accordingly,

$$K_i = \frac{(1 \times 10^{-5}) \times (1 \times 10^{-5})}{1.0}$$

$$= 1 \times 10^{-10}$$

To find the percentage of the acid which is ionized, one need only divide the concentration of ionized acid by the total acid concentration and multiply the resulting quotient by 100, thus,

$$\text{Per cent ionized} = \frac{1 \times 10^{-5}}{1.0} \times 100$$

$$= 1 \times 10^{-3}$$

$$= 0.001\%$$

15.2. Common Ion Effect

Again with reference to a 0.1 M ammonium hydroxide solution, which is 1.3 per cent ionized, suppose that, by adding a soluble salt such as ammonium nitrate, the concentration of ammonium ions is increased from 0.0013 to 1.0013 M. Under these conditions, the number of ammonium ions in the solution is so greatly increased that hydroxyl ions collide with ammonium ions much more frequently than in the original 0.1 M ammonium hydroxide solution. This results in the formation of more un-ionized molecules of NH_4OH, *i.e.*, the reverse reaction in the equilibrium

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

is favored by the increase in the concentration of ammonium ions. Since the concentration of ammonium ions has been increased and because the numerical value of the ionization constant must remain the same, it follows that the concentration of hydroxyl ions must decrease. Accordingly, let m equal that part of the total molarity of OH^- (or NH_4^+) consumed in the establishment of the new equilibrium.

The actual concentrations of ammonium and hydroxyl ions remaining are $(1.0013 - m)$ and $(0.0013 - m)$, respectively; hence,

$$(1.0013 - m) \times (0.0013 - m) = 1.69 \times 10^{-6}$$

$$m = 1.2987 \times 10^{-3}$$

$$= 0.0012987\ M$$

From this it is seen that the concentration of ammonium ions is decreased from 1.0013 M to $1.0013 - 0.0012987 = 1.0000013\ M$, or to a value not much less than 1.0013 M. On the other hand, the concentration of hydroxyl ions is decreased from 0.0013 M to $0.0013 - 0.0012987 = 0.0000013\ M$, a value only one one-thousandth as great as that for the concentration of hydroxyl ions in the 0.1 M ammonium hydroxide solution before addition of the ammonium nitrate.

This case is typical of a situation which is common to all solutions of weak electrolytes and which is usually referred to as the *common ion effect*. If to a solution of a weak electrolyte one adds a strong electrolyte which furnishes an ion in common with one of the products of the ionization of the weak electrolyte, a new equilibrium mixture containing more un-ionized molecules of the weak electrolyte results. The concentration of the noncommon ion is decreased to an extent that is dependent only upon the quantity of the common ion introduced.

A little reflection, and if necessary a few simple calculations, leads to the conclusion that the ammonium hydroxide–ammonium nitrate solution considered above is one that would be relatively insensitive to changes in hydroxyl-ion concentration. One might, for example, attempt to increase $[OH^-]$ by adding more NH_4OH. Owing to the high concentration of ammonium ions from the ammonium nitrate, however, the net effect of this change would be very small. The added OH^- would largely react with the NH_4^+ already present at high concentration to form more un-ionized NH_4OH molecules. Any such solution which contains a weak base or acid in the presence of a salt of a weak base or acid is called a *buffer solution*, and the salt is called a *buffer*. These particular terms are used because of the manner in which the salt acts as a buffer against marked changes in hydrogen-ion (or hydroxyl-ion) concentration upon further addition of limited quantities of either acid or base. A further illustration of buffer solutions is given in the next section.

Applications of the Common Ion Effect. It is common practice to take advantage of the common ion effect in exercising control over the concentrations of ions in solutions. Suppose that for some par-

ticular purpose one wished to use 0.1 M acetic acid but found that the concentration of hydrogen ions in this solution was too great for the purpose at hand. Since acetic acid ionizes as follows,

$$HC_2H_3O_2 \rightleftharpoons H^+ + (C_2H_3O_2)^-$$

the addition of the strong electrolyte sodium acetate (a salt of a weak acid) would serve to increase the concentration of acetate ions. This would lead to a new equilibrium mixture containing more un-ionized molecules of $HC_2H_3O_2$, thus decreasing the concentration of hydrogen ions.

Since a 0.1 M acetic acid solution is about 1.3 per cent ionized at the temperature in question, the concentration of hydrogen ions is 1.3×10^{-3} M, *i.e.*,

$$[H^+] = 0.1 \times 0.013$$
$$= 1.3 \times 10^{-3}$$

The ionization constant for acetic acid (calculated as illustrated above) is 1.8×10^{-5}:

$$\frac{[H^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8 \times 10^{-5}$$

One may now raise the question as to how great $[H^+]$ would be if solid sodium acetate (a strong electrolyte) were added in a quantity such that the 0.1 M acetic acid solution is also 0.2 M with respect to $NaC_2H_3O_2$. By solving the equilibrium-constant expression for $[H^+]$,

$$[H^+] = \frac{(1.8 \times 10^{-5}) \times [HC_2H_3O_2]}{[C_2H_3O_2^-]}$$

assuming that the sodium acetate is completely ionized, and substituting the appropriate concentration values,

$$[H^+] = \frac{(1.8 \times 10^{-5}) \times 0.1}{0.2}$$

and solving, one finds that

$$[H^+] = 9 \times 10^{-6}\ M$$

Thus, the addition of the specified quantity of sodium acetate lowers the hydrogen-ion concentration (by the common ion effect) from 0.0013 M to the much lower value 0.000009 M. Sodium acetate is a salt of a weak acid and therefore acts as a buffer. Consequently the solution that is 0.1 M in $HC_2H_3O_2$ and 0.2 M in $NaC_2H_3O_2$ would maintain substantially the same hydrogen-ion concentration even though more acid were added.

If, in the foregoing case, some particular hydrogen-ion concentration had been desired, calculations similar to those illustrated could be made to determine the weight of sodium acetate required to lower the concentration of hydrogen ions to any desired value.

In the systematic procedures of chemical analysis, advantage is often taken of the common ion effect in preventing the undesirable *partial* precipitation of certain ions from their solutions. This situation may be illustrated by the case of magnesium ions. If, to a solution of magnesium nitrate, or any other soluble magnesium salt, one adds ammonium hydroxide solution, the concentration of hydroxyl ions supplied by the ionization of NH_4OH is sufficient to permit the occurrence of the reaction,

$$Mg^{++}(NO_3)_2^- + 2NH_4OH \rightleftharpoons \underline{Mg(OH)_2} + 2NH_4^+NO_3^-$$

A white precipitate of insoluble magnesium hydroxide[1] appears, but under these conditions only a part of the magnesium ions in the solution are converted to insoluble magnesium hydroxide. The precipitation reaction initially proceeds rapidly but becomes progressively slower until finally equilibrium is established before the forward reaction can reach completion. The reason for this behavior lies in the fact that for every molecule of magnesium hydroxide formed there are formed also two molecules of the strong electrolyte $NH_4^+NO_3^-$. Thus, as the formation of magnesium hydroxide proceeds, the $[NH_4^+]$ is progressively increased, and this, by the common ion effect, operates to depress the ionization of ammonium hydroxide to such a point that the $[OH^-]$ becomes insufficient to permit further formation of magnesium hydroxide. In chemical analysis, *partial* precipitation of any ion is usually undesirable. Hence, it would be better to prevent entirely the precipitation of Mg^{++} as the insoluble hydroxide. This can be accomplished by adding, in advance, an ammonium salt such as ammonium nitrate. If this is done before addition of ammonium hydroxide, the $[NH_4^+]$ is so great that the resulting $[OH^-]$ is too small to permit formation of any insoluble magnesium hydroxide.

15.3. Hydrolysis

The term *hydrolysis* is used to describe certain reactions in which water is one of the reactants. Water is a very weak electrolyte which ionizes as follows:

$$H_2O \rightleftharpoons H^+ + OH^-$$

[1] The formula of magnesium hydroxide is underscored to indicate that it is an insoluble solid.

At 25°C., the concentration of hydrogen ions in pure water is 0.0000001 or 1×10^{-7} M, and since the two ions are formed always in equivalent amounts, the concentration of hydroxyl ions has the same value. Hence, the ion product constant is

$$[H^+] \times [OH^-] = K_i$$

$$(1 \times 10^{-7}) \times (1 \times 10^{-7}) = K_i$$

$$1 \times 10^{-14} = K_i$$

Since this value for the ion product is maintained in aqueous solutions, any factor that changes the concentration of either of these ions results in a corresponding change in the concentration of the other, but in an opposite direction. Thus, a water solution which is 1 M with respect to hydroxyl ions must be 1×10^{-14} M with respect to hydrogen ions since

$$[H^+] \times [OH^-] = 1 \times 10^{-14}$$

$$1 \times [OH^-] = 1 \times 10^{-14}$$

$$[OH^-] = 1 \times 10^{-14}$$

Conversely, if a water solution is 1 M with respect to hydroxyl ions, it must be 10^{-14} M with respect to hydrogen ions.

When solid potassium cyanide is added to pure water, a reaction of hydrolysis ensues, and the salt is said to be *hydrolyzed.*

$$K^+CN^- + HOH \rightleftharpoons K^+OH^- + HCN$$

It should be observed that this and other reactions involving hydrolysis are essentially the reverse of the corresponding neutralization reactions. Thus, in the preceding example, a salt and water react to form a strong base and a weak acid. By virtue of the occurrence of this reaction, the $[H^+]$ is decreased, because hydrogen ions are bound up in the form of extremely slightly ionized molecules of hydrocyanic acid (HCN). Furthermore, the inherent slight degree of ionization of HCN is rendered still less extensive owing to a common ion effect brought about by the high $[CN^-]$ furnished by the strong electrolyte potassium cyanide. Direct experimental measurement of the concentration of hydrogen ions in a water solution of potassium cyanide shows that $[H^+] = 1 \times 10^{-10}$ M. Since the $[H^+]$ has been decreased, the $[OH^-]$ must increase, and the numerical value of the $[OH^-]$ must be such that the ion product of water is maintained, *i.e.*,

$$[H^+] \times [OH^-] = 1 \times 10^{-14}$$

$$(1 \times 10^{-10}) \times [OH^-] = 1 \times 10^{-14}$$

$$[OH^-] = \frac{1 \times 10^{-14}}{1 \times 10^{-10}}$$

$$[OH^-] = (1 \times 10^{-14}) \times (1 \times 10^{10})$$

$$[OH^-] = 1 \times 10^{-4}\ M$$

When the concentration of hydroxyl ions reaches this value, the ionization of water is depressed to such an extent that further hydrolysis of the potassium cyanide cannot occur. Thus, the extent of hydrolysis of KCN is dependent upon the extent to which *un-ionized* molecules of HCN are formed.

When sodium acetate is hydrolyzed,

$$Na^+C_2H_3O_2^- + HOH \rightleftharpoons Na^+OH^- + HC_2H_3O_2$$

the actual extent to which hydrolysis occurs before equilibrium is established is less than in the case of KCN, because $HC_2H_3O_2$ is a stronger acid than HCN and is therefore less effective in tying up the hydrogen ions provided by the ionization of water. Accordingly, in the case of sodium acetate, the $[H^+]$ is greater, and the required increase in the $[OH^-]$ (to permit maintenance of the value of 1×10^{-14} for the ion product of water) is less; hence, sodium acetate is less extensively hydrolyzed than potassium cyanide.

Hydrolysis in Relation to Types of Salts. It is apparent from the preceding examples that the occurrence and the extent of hydrolysis are related to the nature of the acid and base which might be considered as the "parents" of the particular salt. Fortunately, it is possible to consider hydrolysis in terms of such relationships.

1. *Salts of Strong Acids and Strong Bases.* Ordinarily sodium chloride might be expected to hydrolyze as follows:

$$Na^+Cl^- + HOH \rightleftharpoons Na^+OH^- + H^+Cl^-$$

However, the products Na^+OH^- and H^+Cl^- are both strong electrolytes, and the ions of each are essentially equally highly active. Consequently, the occurrence of this reaction could produce nothing that would result in any unbalancing of either the $[H^+]$ or the $[OH^-]$ corresponding to that of pure water. Hence, in a water solution of sodium chloride, $[H^+] = [OH^-] = 1 \times 10^{-7}$; the ion product constant is essentially the same as that for pure water, and this leads to the conclusion

that there is no reason why such a salt should hydrolyze. **Salts of strong acids and strong bases are not appreciably hydrolyzed.**

2. *Salts of Strong Bases and Weak Acids.* As has already been shown in the case of potassium cyanide and sodium acetate, **salts of strong bases and weak acids hydrolyze to form basic solutions.** In any given case, the extent of hydrolysis is inversely proportional to the ionization constant of the weak acid formed in the hydrolytic reaction. In general, the weaker the acid that is formed, the greater is the extent of hydrolysis.

3. *Salts of Weak Bases and Strong Acids.* The hydrolysis of a salt such as ammonium chloride would be expected to occur as shown by the equilibrium,

$$NH_4^+Cl^- + HOH \rightleftharpoons NH_4OH + H^+Cl^-$$

since hydroxyl ions become bound up in the formation of slightly ionized molecules of the weak base NH_4OH. If the $[OH^-]$ is thereby decreased, hydrolysis must continue until the $[H^+]$ is increased to such a value that the product of these two ion concentrations is equal to 1×10^{-14}. Thus, the extent of hydrolysis of a salt of a weak base and a strong acid is inversely proportional to the ionization constant of the weak base; *i.e.*, the weaker the base that is formed in the hydrolytic reaction, the greater is the extent of hydrolysis. **Salts of weak bases and strong acids hydrolyze to form acidic solutions.** This generalization applies equally well to bases such as $Fe(OH)_3$, $Bi(OH)_3$, and $Cu(OH)_2$, which are weak bases by virtue of the fact that they are practically insoluble in water and hence provide relatively low $[OH^-]$.

4. *Salts of Weak Acids and Weak Bases.* The equation for the reaction between ammonium acetate and water,

$$NH_4^+C_2H_3O_2^- + HOH \rightleftharpoons NH_4OH + HC_2H_3O_2$$

shows that the products consist of a weak acid and a weak base, both of which are ionized to essentially the same extent. For this reason, the ionization equilibrium of water is progressively displaced to the right to provide H^+ and OH^-, which are subsequently utilized in the formation of slightly ionized molecules of acetic acid and ammonium hydroxide. The hydrolysis proceeds far toward completion since neither a high $[H^+]$ nor a high $[OH^-]$ is produced to prevent further hydrolysis. Accordingly, it is seen that salts of weak acids and weak bases are extensively hydrolyzed to form neutral, weakly basic, or weakly acidic solutions, depending on the relative "strengths" of the parent acids and bases.

Quantitative Aspects of Hydrolysis. The hydrolysis of sodium acetate, a salt of a strong base (Na^+OH^-) and a weak acid ($HC_2H_3O_2$), serves as a typical example of this type of reaction.

$$Na^+C_2H_3O_2^- + HOH \rightleftharpoons Na^+OH^- + HC_2H_3O_2$$

The equilibrium constant for a hydrolytic equilibrium is commonly designated as K_h; thus for the foregoing equilibrium,

$$K_h = \frac{[Na^+] \times [OH^-] \times [HC_2H_3O_2]}{[Na^+] \times [C_2H_3O_2^-] \times [H_2O]}$$

Another convention that is based simply upon convenience is the designation of the ion product constant of water as K_w; this practice is mentioned here because of the frequency with which this term is used in calculations related to equilibria involving hydrolysis.

Calculations concerned with hydrolytic equilibria are fundamentally no different from those related to other equilibria. As an added illustration, however, suppose that one wished to know the hydroxyl-ion concentration and the concentration of un-ionized acetic acid that are present in a 0.01 M sodium acetate solution. These calculations are simplified by assuming that the sodium acetate is completely ionized; it is further necessary to know that the ionization constant of acetic acid is 1.8×10^{-5} and that the ion product constant of water is 1×10^{-14}.

Inspection of the expression for the hydrolysis constant for sodium acetate shows that cancellation of the term common to both numerator and denominator (*i.e.*, $[Na^+]$) and multiplication of both numerator and denominator by $[H^+]$ gives an expression

$$K_h = \frac{[HC_2H_3O_2] \times [OH^-]}{[C_2H_3O_2^-]} \times \frac{[H^+]}{[H^+]}$$

the numerator of which contains the two terms that appear in K_w. The remainder of the K_h expression is the reciprocal of the ionization constant for acetic acid. Accordingly,

$$K_h = \frac{K_w}{K_i}$$

and since the values for K_w and K_i are known, it follows that

$$K_h = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}}$$
$$= 5.5 \times 10^{-10}$$

It is now established that

$$\frac{[OH^-] \times [HC_2H_3O_2]}{[C_2H_3O_2^-]} = 5.5 \times 10^{-10}$$

and inspection of the equation for the hydrolysis equilibrium shows that $[OH^-] = [HC_2H_3O_2]$, because the hydrolysis of 1 mole of sodium acetate produces 1 mole of hydroxyl ion and 1 mole of acetic acid. Consequently,

$$\frac{[OH^-]^2}{[C_2H_3O_2^-]} = 5.5 \times 10^{-10}$$

and since $[C_2H_3O_2^-]$ is specified initially as 0.01 M,

$$\frac{[OH^-]^2}{0.01} = 5.5 \times 10^{-10}$$

$$[OH^-]^2 = 5.5 \times 10^{-12}$$

$$[OH^-] = 2.3 \times 10^{-6}\ M$$

which is one of the values sought. Since the concentration of hydroxyl ion and the concentration of un-ionized acetic acid are equal,

$$[HC_2H_3O_2] = 2.3 \times 10^{-6}\ M$$

15.4. Acid-base Reactions

Although the nature of acids and bases has already been discussed (Chap. 12; see also Sec. 17.8), certain aspects of acid-base reactions may be considered profitably in terms of a considerably different point of view.

Brφnsted Theory. In view of the fact that pure gaseous hydrogen chloride is a predominantly covalent compound which does not possess the properties of an acid, there should be some means of explaining why a water solution of hydrogen chloride (hydrochloric acid) exhibits the properties of a solution of a strong electrolyte and is strongly acidic.

An explanation may be provided on the basis of a theory proposed by Brønsted (Fig. 71) in 1923. The characteristic feature of this theory is that it broadens one's viewpoint to the extent of including as acids and bases many substances not previously classified under these headings. In terms of Brønsted's views, when HCl is dissolved in water the following equilibrium is established:

$$HCl + H_2O \rightleftharpoons (H_3O)^+ + Cl^-$$

The acidic properties of the solution are attributed to the ion $(H_3O)^+$, which is known as the hydronium ion and which is considered to be a

hydrated proton, *i.e.*, $H^+ \cdot H_2O$. On this basis, the interaction of sodium hydroxide and hydrochloric acid would be represented by the equation,

$$(H_3O)^+Cl^- + Na^+(OH)^- \rightarrow 2H_2O + Na^+Cl^-$$

The ionization of other acids and their reactions with bases may be represented in a similar manner.

In the light of this point of view, an acid may be defined as any substance (molecule or ion) that is capable of furnishing or donating a hydrogen ion (*i.e.*, a proton). Thus, the HCl is considered to be an acid because it donates a proton to the water molecule in the formation of the hydronium ion. Similarly, a base is defined as any molecule or ion capable of accepting a proton. Accordingly, the water molecule should be classified as a base in these reactions since it unites with (accepts) a proton in the process of forming the hydronium ion.[1] The hydroxyl ion $(OH)^-$, the acetate ion $(C_2H_3O_2)^-$, the carbonate ion $(CO_3)^=$, and in fact any negative ion capable of uniting with hydrogen ions would also be classified as a base.

FIG. 71. J. N. Brønsted (1879–1947). (*Courtesy of The Edgar Fahs Smith Memorial Collection in the History of Chemistry, The University of Pennsylvania.*)

Although useful in explaining many aspects of chemical behavior not otherwise readily understood, the Brønsted theory has certain serious limitations. In this book, the use of these views is limited to those few cases in which the Brønsted theory provides a more satisfactory explanation than can be given on any other basis.

Relative Strengths of Acids and Bases. In terms of the Brønsted theory, the relative strengths of any two acids are dependent upon their relative abilities to act as proton donors. The ionization of

[1] Although a water molecule that accepts a proton should be classed as a base, any water molecule that furnishes a proton must be classed as an acid. Thus, in the ionization of water,

$$2H_2O \rightleftharpoons H_2O^+ + OH^-$$

one water molecule acts as an acid and the other as a base (see Sec. 14.10).

hydrochloric and acetic acids may be represented by the equilibria,

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$

The equilibrium mixture corresponding to the ionization of HCl contains a high concentration of H_3O^+ as compared with a very low concentration of this ion in the acetic acid equilibrium mixture. Consequently, HCl is said to be a stronger acid than $HC_2H_3O_2$ because it is a much more effective proton donor.

When these same equilibria are considered from the standpoint of the relative strengths of the bases involved, it must be recognized that in each case two bases (proton acceptors) are in competition for the proton. In the first instance, the two bases H_2O and Cl^- compete for the proton furnished by HCl, and since the equilibrium mixture is richer in H_3O^+ than in HCl, one must conclude that the water molecule is a stronger base than the chloride ion. Similarly, the acetate ion must be a stronger base than the water molecule because in the acetic acid equilibrium mixture the concentration of $HC_2H_3O_2$ molecules is far greater than the concentration of hydronium ions. Furthermore, it follows that the acetate ion must be a considerably stronger base than the chloride ion.

Effective Acidity versus Total Acidity. Once it is admitted that hydrochloric is a stronger acid than acetic, the question arises as to why the same quantity of base is required to neutralize 1 mole each of these acids. The answer lies in the fact that in either case the neutralization reaction involves the union of the hydronium ion with the hydroxyl ion, which is a base much stronger than Cl^-, $C_2H_3O_2^-$, or H_2O.

$$H_3O^+ + OH^- \rightarrow 2H_2O$$

When a base is added to the ionization equilibrium mixture of either HCl or $HC_2H_3O_2$, the hydronium ions present are effectively removed owing to the occurrence of the foregoing reaction with OH^-. As quickly as this happens, however, more HCl or $HC_2H_3O_2$ molecules react with water molecules to reestablish the equilibrium concentration of H_3O^+, and these ions thereby become available for reaction with additional base. In the case of either the strong or the weak acid, additional hydronium ions become progressively available, and this continues until there are no remaining HCl or $HC_2H_3O_2$ molecules and neutralization is complete. It must be concluded, in comparing any two acids that contain the same number of potential protons, that the

active concentration of hydronium ions may differ greatly and yet the total potential acidity is the same.

Effective Concentration of Hydrogen Ions. Particularly where low acidities are involved, the expression of the $[H^+]$ in terms of normalities is somewhat cumbersome. Thus the $[H^+]$ in pure water is 0.0000001 N and that of a 1 N solution of sodium hydroxide is 0.00000000000001 N. Such values may, of course, be expressed somewhat more simply as 1×10^{-7} N and 1×10^{-14} N, respectively. However, since botanists, biologists, physicians, and others less accustomed to these schemes of notation frequently have need to express effective hydrogen-ion (or hydronium-ion) concentrations, it has been found desirable to adopt a still simpler scheme which has come into wide use in the various branches of chemistry also. Such a scheme is the "pH scale" or "hydrogen-ion index" devised by Sörensen (Fig. 72). In this system, the pH value of a solution is defined by

FIG. 72. S. P. L. Sörensen (1868–1939). (*Courtesy of The Edgar Fahs Smith Memorial Collection in the History of Chemistry, The University of Pennsylvania.*)

$$\text{pH} = \log \frac{1}{[H^+]}$$

Thus for pure water, $[H^+] = 1 \times 10^{-7}$ mole per liter, and the pH value is given by

$$\text{pH} = \log \frac{1}{1 \times 10^{-7}} = \log (1 \times 10^7) = 7$$

If the $[H^+]$ of a solution is known or can be determined experimentally by any one of several available methods, the pH value may be calculated as indicated above. Also, methods have been devised for the fairly accurate direct measurement of acidities in terms of pH values. The relationship between the pH scale and the corresponding acidities expressed in normalities is shown in Table 20. The pH value of the human blood is about 7.2 (*i.e.*, slightly basic) and cannot vary greatly from this value without fatal results. The pH of soils is sometimes regulated by the addition of lime. Cooking, baking, brewing, and

many other operations depend upon regulated acidities usually expressed in terms of pH values.

TABLE 20

RELATION BETWEEN pH VALUES AT 25° AND NORMALITY

Normality with respect to H^+	10^0	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
Corresponding pH values	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14

$H^+ = 1\ N$ ← increasing acidity — neutrality — increasing basicity → $OH^- = 1\ N$

A strictly related term, pOH, is defined as,

$$\text{pOH} = \log \frac{1}{[\text{OH}^-]}$$

For pure water at 25°,

$$\text{pOH} = \log \frac{1}{1 \times 10^{-7}}$$

$$= 7$$

and since

$$K_w = [\text{H}^+] \times [\text{OH}^-]$$

$$= 1 \times 10^{-14}$$

it follows that

$$\text{pH} + \text{pOH} = 14$$

15.5. Precipitation Reactions

Many common laboratory procedures and industrial chemical processes depend upon the occurrence of reactions between ions in solution which result in the formation of insoluble solids, or precipitates. For example, insoluble nickel sulfide is precipitated when a solution containing Ni^{++} is treated with the quantity of sulfide ion required by the equation,

$$Ni^{++} + S^{=} \rightleftharpoons \underline{NiS}$$

At equilibrium, the concentrations of Ni^{++} and $S^{=}$ remaining in the solution are quite low, so that for many purposes the reaction may be considered as having proceeded to completion. Nevertheless, some nickel and sulfide ions do remain in the solution where they exist in equilibrium with the precipitated nickel sulfide (Fig. 73). The actual

concentration of ions remaining in solution (*i.e.*, not precipitated) is, of course, related to the solubility of the substance involved.

Solubility Product. When, as indicated above, a solid (precipitate) is in equilibrium with a saturated solution of its ions, the product of the molar concentrations of these ions in the solution is called the *solubility product*. For nickel sulfide, accurate analysis of a saturated solution of this compound shows that the solution contains 1×10^{-13} mole of Ni^{++} per liter, and since the two ions were brought together at equivalent concentrations, the molar concentration of $S^{=}$ must have the same value. Accordingly, the solubility product of nickel sulfide,

$$[Ni^{++}] \times [S^{=}] = K_{s.p.}$$

is given by

$$(1 \times 10^{-13}) \times (1 \times 10^{-13}) = K_{s.p.}$$

$$K_{s.p.} = 1 \times 10^{-26}$$

The symbol $K_{s.p.}$ is used to designate the *solubility product constant*, which is obviously nothing more than an ion product constant. The solubility product relationship as outlined above is only an approximation which is limited to solutions of slightly soluble substances in which the total ion concentrations are very low. In order for this relationship to hold rigorously, it is necessary to consider not the product of the two concentration terms but rather the product of the activities of the ions. Thus, the $[Ni^{++}]$, for example, would have to be replaced by the product of the nickel-ion concentration and the appropriate activity coefficient; a similar correction also would have to be applied in the case of $[S^{=}]$.

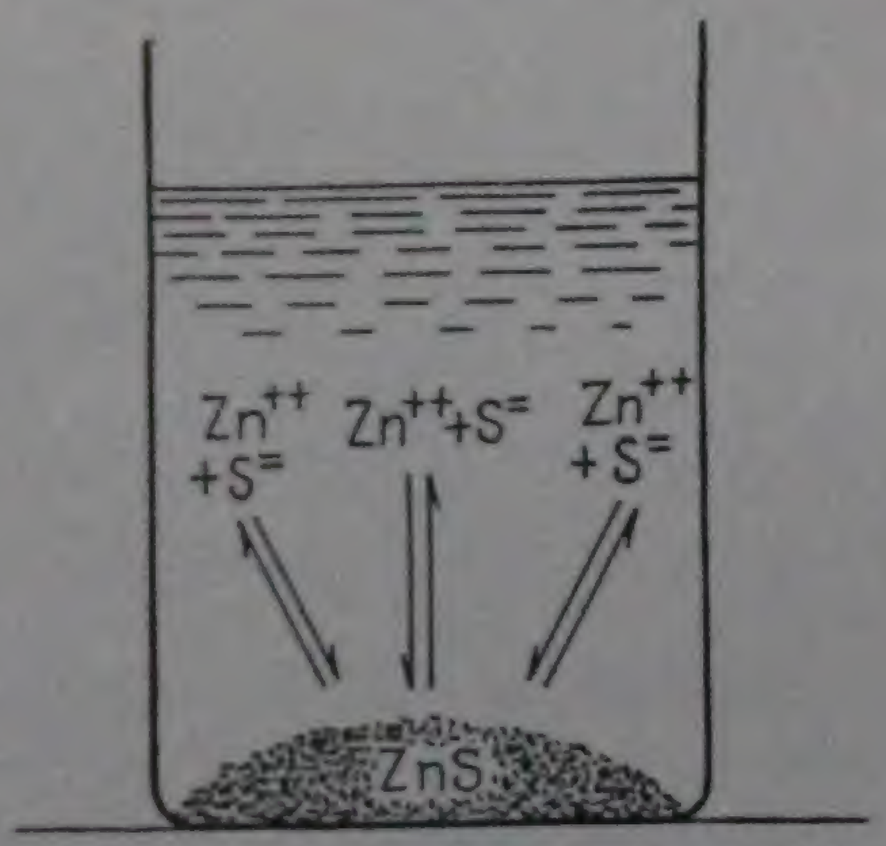

FIG. 73. A precipitate in equilibrium with a solution of its ions.

A low value for $K_{s.p.}$ therefore means low solubility, which in turn implies relatively complete precipitation. For example, the $K_{s.p.}$ for CuS is 4×10^{-38}, or a value very much lower than that for NiS. Consequently, under the same conditions of sulfide-ion concentration, Cu^{++} is precipitated much more nearly completely than Ni^{++}. A tabulation of $K_{s.p.}$ values for various substances is given in the Appendix.

When a solution containing $S^{=}$ is added slowly to a solution containing Cu^{++}, for example, precipitation does not begin until the product of the molar concentrations of Cu^{++} and $S^{=}$ is sufficient to exceed the solubility product constant of CuS. Once this requirement is met,

the degree to which precipitation proceeds toward completion is dependent upon the extent to which the $K_{s.p.}$ value is exceeded. If it is desired to precipitate Cu^{++} as nearly completely as possible, an excess of $S^{=}$ should be added. Under these conditions the ion product

$$[Cu^{++}] \times [S^{=}] = K_{s.p.} = 4 \times 10^{-38}$$

is maintained while, as the sulfide-ion concentration is progressively increased, the copper-ion concentration is decreased to a minimum. It is for this reason that an excess of a precipitating agent is usually added.

In qualitative chemical analysis, numerous ions are precipitated by means of hydrosulfuric acid (H_2S). This is a weak acid which is soluble in pure water at room temperature to an extent such that the saturated solution is approximately 0.1 *M*. The ion product constant for the saturated solution is

$$[H^{+}]^2 \times [S^{=}] = 1.1 \times 10^{-23}$$

and the utility of this reagent commonly depends upon the fact that $[S^{=}]$ may be regulated by proper adjustment of $[H^{+}]$. Thus, in the saturated aqueous solution, $[S^{=}] = 1 \times 10^{-15}$, but if the solution is made 0.1 *M* in H^{+}, the $[S^{=}]$ is decreased to 1×10^{-21}.

It is often convenient, if not indeed necessary, to know whether a given ion will precipitate under specified conditions of sulfide-ion concentration. Such decisions can be reached if the solubility product constants are known. For example, the question may arise as to whether MnS would precipitate from a solution in which $[Mn^{++}] = 1 \times 10^{-1}$, $[H^{+}] = 1 \times 10^{-1}$, and which is saturated with H_2S at 25°. Since $K_{s.p.}$ for MnS is about 1×10^{-15}, it may be shown that precipitation does not occur under the conditions specified. Owing to the effect of the common ion, H^{+}, the $[S^{=}] = 1 \times 10^{-21}$, and

$$[Mn^{++}] \times [S^{=}] = (1 \times 10^{-1}) \times (1 \times 10^{-21})$$
$$= 1 \times 10^{-22}$$

which is a value much less than $K_{s.p.}$ for MnS. Accordingly, it is seen that too low a concentration of sulfide ion has been provided to exceed the solubility product of MnS. If, however, the solution in question had been made 1×10^{-1} *M* with respect to the strong electrolyte $(NH_4)_2^{+}S^{=}$, which may be assumed to be completely ionized, then

$$[Mn^{++}] \times [S^{=}] = (1 \times 10^{-1}) \times (1 \times 10^{-1})$$
$$= 1 \times 10^{-2}$$

which is a value very much greater than $K_{s.p.}$ for MnS. Under these conditions precipitation of MnS occurs, and since 1×10^{-2} is so much greater than 1×10^{-15}, the precipitation reaction proceeds essentially to completion.

As indicated previously, the solubility product generalization holds for any slightly soluble substance. It should be recognized also that the equilibrium between the solid and its saturated solution need not be approached through a precipitation reaction. Exactly the same principles are involved when, for example, a slightly soluble salt is agitated with water until the solution becomes saturated with the salt in question. If one should saturate some water with lead sulfate at 40°, one would find that the resulting saturated solution contained 0.056 g. of $PbSO_4$ per liter of solution. Since the molecular weight of lead sulfate is 303, the corresponding molar concentration is $0.056 \div 303 = 1.84 \times 10^{-4}\ M$. This is also the molar concentration of Pb^{++} and $SO_4^{=}$, since this salt is a strong electrolyte and may be considered as completely ionized. Accordingly, the solubility product constant for lead sulfate is

$$\begin{aligned} K_{s.p.} &= [Pb^{++}] \times [SO_4^{=}] \\ &= (1.84 \times 10^{-4}) \times (1.84 \times 10^{-4}) \\ &= 3.4 \times 10^{-8} \end{aligned}$$

Another type of calculation that is commonly encountered is illustrated by the following example. If the solubility product of cuprous chloride is

$$K_{s.p.} = [Cu^{+}] \times [Cl^{-}] = 1 \times 10^{-6}$$

and the concentration of Cu^{+} in a certain solution is known to be 0.0125 M, what is the greatest concentration of chloride ion that can be present without the occurrence of precipitation? From the solubility product expression,

$$\begin{aligned} [Cl^{-}] &= \frac{1 \times 10^{-6}}{[Cu^{+}]} \\ &= \frac{1 \times 10^{-6}}{0.0125} \\ &= 8.0 \times 10^{-5}\ M \end{aligned}$$

At this chloride-ion concentration, the solubility product of cuprous chloride is equaled but not exceeded; consequently precipitation does not occur.

GENERAL EXERCISES

1. Distinguish between the following terms: (*a*) equilibrium constant, ion product constant, hydrolysis constant, and solubility product constant; (*b*) hydrolysis and neutralization; (*c*) total acidity and effective concentration of hydrogen ions.

2. Why is the ionization of strong electrolytes not represented as an equilibrium as in the case of weak electrolytes?

3. How is the common ion effect related to the law of mass action?

4. What determines the *extent* to which a salt undergoes hydrolysis?

5. List four classes of salts, and indicate (*a*) whether each hydrolyzes upon contact with water and (*b*) the nature of the resulting solution in each case.

6. In terms of the Brønsted theory, show that water may be looked upon either as an acid or a base.

7. Why does the term $[H_2O]$ not appear in the calculation of the hydrolysis constant for sodium acetate (see Sec. 15.3)?

8. Two solutions are prepared so that one contains 36.457 g. of HCl and the other 97 g. of HSO_4^-. How do these two solutions compare as to (*a*) effective $[H^+]$ and (*b*) total available acidity?

9. How would the $[OH^-]$ in an aqueous solution of ammonia be influenced by an elevation of the temperature?

10. When two solutions containing solutes that react to form a sparingly soluble substance are brought together, what requirement must be met if the insoluble substance is to appear as a precipitate?

11. Suggest an alternative formula for the hydrate $CuSO_4 \cdot 5H_2O$.

12. Which of the following solutions would provide the greater $[Hg^{++}]$: (*a*) a 0.1 *M* solution of mercuric chloride, or (*b*) a 0.1 *M* solution of mercuric chloride containing some dissolved sodium chloride?

PROBLEMS

1. Calculate the ionization constant for acetic acid corresponding to the temperature at which a 0.1 *M* solution of this acid is 1.36 per cent ionized.

2. Benzoic acid is a common organic acid which may be represented by the formula HBz and which ionizes as follows: $HBz \rightleftharpoons H^+ + Bz^-$. (*a*) If the ionization constant of this acid is 6.6×10^{-5}, calculate the hydrogen-ion concentration in a 0.12 *M* solution of benzoic acid in water. (*b*) Calculate the percentage ionization.

3. If a 0.01 *M* solution of ammonium hydroxide is 4.47 per cent ionized at 40°C., calculate the ionization constant.

4. In a certain aqueous solution of hydrocyanic acid the acid is 0.014 per cent ionized. If the ionization constant is 2.1×10^{-9}, what is the molar concentration of HCN in the solution?

5. Three-tenths of a mole of solid sodium acetate (which may be assumed to be completely ionized) is dissolved in 1 liter of 0.1 *M* acetic acid solution. If the ionization constant of acetic acid is 1.8×10^{-5}, what is the concentration of hydrogen ions in this solution?

6. Calculate the concentration of hydroxyl ions in a 0.17 *M* ammonium hydroxide solution, which is 0.25 per cent ionized.

7. If one dissolves 0.063 mole of solid ammonium chloride (assumed to be completely ionized) in 1 liter of 0.1 M ammonium hydroxide solution, what is the hydroxyl-ion concentration in the resulting solution? (K_i for NH_4OH is given in Prob. 6.)

8. If ammonium acetate is 80 per cent ionized, at what concentration must this salt be present in 0.5 M acetic acid solution in order to provide a hydrogen-ion concentration of 2.8×10^{-5} M? (K_i for $HC_2H_3O_2$ is given in Prob. 5.)

9. Calculate the molar concentration of acetate ion required to lower $[H^+]$ in a 0.025 M acetic acid solution to a value of 4×10^{-6} M.

10. If 15.4 g. of solid ammonium acetate (assumed to be 100 per cent ionized) and 5.0 ml. of 7.0 M acetic acid are dissolved in enough water to make a total volume of 400 ml., what is the concentration of hydrogen ions in the resulting solution?

11. What is (*a*) the hydroxyl-ion concentration, and (*b*) the pH, of a solution in which $[H^+] = 1 \times 10^{-5}$ M?

12. Calculate the hydrogen-ion concentration and pH for each of the following solutions: (*a*) 0.01 M sodium hydroxide, (*b*) 0.0001 M sodium hydroxide, (*c*) 0.1 M hydrochloric acid, (*d*) 0.001 M nitric acid, (*e*) 0.100 M potassium hydroxide.

13. The ionization constant for phenol (an organic compound commonly known as "carbolic acid," which may be represented by the formula HA) is 1×10^{-10}. What is the pH of a 0.016 M aqueous solution of this substance?

14. What is the pH of solutions in which (*a*) $[H^+] = 5 \times 10^{-12}$ M, (*b*) $[H^+] = 6.3 \times 10^{-4}$ M?

15. Calculate $[H^+]$ and pOH for solutions that have the following pH values: (*a*) 8.6, (*b*) 2.07.

16. Determine (*a*) pH, (*b*) $[OH^-]$, and (*c*) pOH for a solution which is 7.75×10^{-4} M with respect to H^+.

17. If K_i for HCN is 7×10^{-10} and K_w is 1×10^{-14}, calculate (*a*) K_h for 0.2 M potassium cyanide, and (*b*) the $[OH^-]$ in this solution.

18. Given the information that K_i for acetic acid is 1.8×10^{-5}, calculate the per cent hydrolysis in each of the following cases: (*a*) 0.001 M sodium acetate, (*b*) 1.0 M sodium acetate.

19. K_i for nitrous acid $= 5 \times 10^{-4}$ and $K_w = 1 \times 10^{-14}$. Calculate (*a*) K_h for 0.62 M KNO_2, and (*b*) the corresponding $[OH^-]$.

20. If $K_{s.p.}$ for ZnS $= 1.2 \times 10^{-23}$, what is the solubility (expressed in molarity) of zinc sulfide in a solution in which $[S^=] = 0.25$ M?

21. If the concentration of sulfide ion in a given solution is 1.1×10^{-22} M, what is the maximum concentration of Pb^{++} that may be present without the occurrence of precipitation of PbS? ($K_{s.p.}$ for PbS $= 3.4 \times 10^{-28}$.)

22. The solubility of silver carbonate in water at 20° is 0.03 g. per liter. Calculate $K_{s.p.}$ for this salt.

23. A 0.1 M solution of copper nitrate is made 0.1 M in H^+ and saturated with H_2S. Show that $K_{s.p.}$ for CuS ($= 4 \times 10^{-38}$) is exceeded under these conditions.

24. A solution is prepared such that $[NiSO_4] = 0.1$ M, and $[S^=] = 1.3 \times 10^{-15}$. If $K_{s.p.}$ for NiS $= 1 \times 10^{-26}$, make calculations which show whether nickel sulfide is precipitated.

25. If $K_{s.p.}$ for MnS $= 1.4 \times 10^{-15}$, determine whether precipitation of manganous sulfide occurs from a solution in which $[S^=] = 1.9 \times 10^{-22}$ and $[Mn^{++}] = 2.7$ M.

26. A solution contains the following ions at the indicated concentrations: $[H^+] = 3.0\ M$, $[S^=] = 1 \times 10^{-24}\ M$, and $[Pb^{++}] = 3.2 \times 10^{-4}\ M$. If $K_{s.p.}$ for $PbS = 3.4 \times 10^{-28}$, make calculations necessary to show whether PbS precipitates from this solution.

SUGGESTED READING

Journal of Chemical Education

Dow, The Equilibrium Constant Equation, **17,** 439 (1940).
Radimer, Solution of Problems Involving Equilibrium Constants, **27,** 251 (1950).
O'Brien and Kenny, The Hydrolysis of a Salt Derived from a Weak Acid and Weak Base, **16,** 140 (1939).
Foster, Hydrolysis and Its Relation to Ionic Charge and Radius, **17,** 509 (1940).
Kilpatrick, Acids, Bases, and Salts, **12,** 109 (1935).
Hazlehurst, Acid-base Reactions, **17,** 466 (1940).
Hazlehurst, Pictures of Acid-base Reactions, **17,** 374 (1940).
Alyea, A Résumé of the Proton Transfer Concept of Acids and Bases, **18,** 206 (1941).
Ginell, Acids and Bases: A Critical Reevaluation, **20,** 250 (1943).
Ashley, Hydrogen Ion Concentration, **5,** 1647 (1928).
Kilpatrick and Kilpatrick, The Definition of pH, **9,** 1010 (1932).
Gorman, A Review of the Interpretation of pH, **17,** 343 (1940).
French, pH Determinations in Elementary Chemistry, **13,** 534 (1936).
Taylor, The Application of pH Control, **6,** 36 (1929).
McAlpine, Changes in pH at the Equivalence Point, **25,** 694 (1948).
Denbigh, The Theory of Solubility Product, **18,** 126 (1941).
Zuffanti, Solubility Product, **17,** 433 (1940).

Science

MacInnes, Criticism of a Definition of pH, **108,** 693 (1948).

CHAPTER 16

CLASSIFICATION OF THE ELEMENTS

In view of the fact that nearly 100 chemical elements are now known, one is at once impressed by the fact that the acquisition of a detailed knowledge of the chemical and physical properties of each of these elements would be an extremely arduous task. Fortunately, however, it is not necessary for most purposes to study all these elements in terms of their individual characteristics. Over a long period of time and as a composite result of the efforts of many scientists, it is possible to study the elements largely in terms of the interrelationships that they exhibit. On the other hand, one must not lose sight of the fact that, for some purposes, each individual element must be made the subject of very detailed study.

16.1. Historical

In the early years of the nineteenth century, chemists began to observe certain types of similarity among some of the elements known at that time. At first these observations were restricted to as few as three elements but later were expanded to include as many as sixty. Döbereiner, Newlands, De Chancourtois, and others attempted with only very limited success to organize the known elements in terms of their atomic weights and thereby to provide a basis for the correlation of their properties. The first major accomplishment along these lines came as a result of the work of the German Lothar Meyer and the Russian Mendelyeev (Fig. 74). Although they should be given joint credit for having quite independently devised the first reasonably satisfactory classification of the elements, Mendelyeev's work received much greater attention because of the boldness and almost uncanny accuracy of the predictions that he made with reference to the existence and properties of elements not then known.

Mendelyeev arranged the known elements in ascending order of their atomic weights. He observed that same sort of periodic recurrence of properties that was pointed out earlier by Newlands. This periodicity in chemical and physical properties may be likened to the

periodic recurrence of the four seasons. Thus, each recurring summer season has detailed characteristics which are similar to (but not necessarily identical with) those of the preceding and following summer seasons. Just as two summer seasons are separated by three other and different seasons, so any two related elements are separated by a number of intervening elements having different properties.

The success of the Mendelyeev classification was necessarily limited by the lack of a basis of classification more fundamental than atomic weights. Such was ultimately provided largely as the result of the

FIG. 74. D. I. Mendelyeev (1834–1907). (*Courtesy of The Edgar Fahs Smith Memorial Collection in the History of Chemistry, The University of Pennsylvania.*)

work of Moseley (Secs. 4.2 and 4.4), which made possible a classification in terms of atomic numbers. Thereupon, certain ambiguities inherent in the Mendelyeev classification were eliminated. A modern version of the *periodic arrangement of the elements* or *periodic table* of the type devised by Mendelyeev is shown in Fig. 75. In this table the elements are arranged in order of ascending atomic numbers in accordance with the *periodic law*, which is stated as follows: **The properties of the elements are periodic functions of their atomic numbers.** The manner in which these periodic recurrences of properties may be correlated with structural similarity of the atoms involved has already been shown in Fig. 17. A comparison of Figs. 17 and 75 shows that the two are identical through atomic numbers 1 to 20 inclusive; it follows that they would continue to be identical if Fig. 17 were extended to include the elements of higher atomic numbers.

Period	Group 0	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII		
1		1 H = 1.0080									
2	2 He = 4.003	3 Li = 6.940	4 Be = 9.013	5 B = 10.82	6 C = 12.010	7 N = 14.008	8 O = 16.0000	9 F = 19.00			
3	10 Ne = 20.183	11 Na = 22.997	12 Mg = 24.32	13 Al = 26.97	14 Si = 28.06	15 P = 30.98	16 S = 32.066	17 Cl = 35.457			
4	18 A = 39.944	19 K = 39.096	20 Ca = 40.08	21 Sc = 45.10	22 Ti = 47.90	23 V = 50.95	24 Cr = 52.01	25 Mn = 54.93	26 Fe = 55.85	27 Co = 58.94	28 Ni = 58.69
		29 Cu = 63.54	30 Zn = 65.38	31 Ga = 69.72	32 Ge = 72.60	33 As = 74.91	34 Se = 78.96	35 Br = 79.916			
5	36 Kr = 83.7	37 Rb = 85.48	38 Sr = 87.63	39 Y = 88.92	40 Zr = 91.22	41 Nb = 92.91	42 Mo = 95.95	43 Tc = 99	44 Ru = 101.7	45 Rh = 102.91	46 Pd = 106.7
		47 Ag = 107.880	48 Cd = 112.41	49 In = 114.76	50 Sn = 118.70	51 Sb = 121.76	52 Te = 127.61	53 I = 126.92			
6	54 Xe = 131.3	55 Cs = 132.91	56 Ba = 137.36	57 La = 138.92	72 Hf = 178.6	73 Ta = 180.88	74 W = 183.92	75 Re = 186.31	76 Os = 190.2	77 Ir = 193.1	78 Pt = 195.23
		79 Au = 197.2	80 Hg = 200.61	81 Tl = 204.39	82 Pb = 207.21	83 Bi = 209.00	84 Po = 210	85 At = 210			
7	86 Rn = 222	87 Fr = 223	88 Ra = 226.05	89 Ac = 227							

Rare-earth series	1	58 Ce = 140.13	59 Pr = 140.92	60 Nd = 144.27	61 Pm = 147	62 Sm = 150.43	63 Eu = 152.0	64 Gd = 156.9
		65 Tb = 159.2	66 Dy = 162.46	67 Ho = 164.94	68 Er = 167.2	69 Tm = 169.4	70 Yb = 173.04	71 Lu = 174.99
	2	90 Th = 232.12	91 Pa = 231	92 U = 238.07	93 Np = 237	94 Pu = 239	95 Am = 241	96 Cm = 242
		97 Bk	98 Cf	99	100	101	102	103

FIG. 75. Modern Mendelyeev-type periodic table.

16.2. General Relations of the Mendelyeev Arrangement

When arranged in order of ascending atomic numbers, the elements may be listed (Fig. 75) in tabular form subdivided into nine vertical columns which are known as *groups* and seven horizontal rows which are called *periods*. The detailed character of these groups and periods are considered after some ideas concerned with the over-all relationships of the periodic table have been pointed out.

An examination of the elements listed in any given group shows that these elements exhibit certain marked similarities in properties and certain more or less regular trends in both chemical and physical characteristics. Regularities and relationships of a somewhat different character are observed when one examines the properties of the elements that fall into any given horizontal period.

Metals, Nonmetals, and Metalloids. If a diagonal line is drawn across the table, as shown in Fig. 75, and if Group VIII is neglected for the moment, the following general relations become apparent:

1. The elements tabulated below and to the left of the diagonal line are those having the properties of metals. Furthermore, for the elements in any given vertical group, the farther removed from the diagonal line the more pronounced is the metallic character of the element. Thus the most metallic elements are listed in the lower left-hand region of the table.

2. The elements tabulated above and to the right of the diagonal line are those which, in general, do not possess any marked degree of metallic character and hence are known as the *nonmetals*. Nonmetallic character becomes more pronounced in those elements allocated to positions above and to the right of the diagonal line, with the result that the most nonmetallic elements are found in the upper right-hand region of the table.

3. If the upper right-hand region (nonmetals) and the lower left-hand region (metals) contain elements that represent the two extremes in metallic and nonmetallic character, then it follows that the diagonal line represents a line of demarcation between these two broad classes of elements. Accordingly, it is not surprising to find that the elements located on or near this line are those which are intermediate in character between the metals and the nonmetals. These elements are called *semimetals* or *metalloids*. For example, the element arsenic exhibits some properties that are characteristic of the metals and certain other properties that are most commonly possessed by nonmetals. In some of its chemical changes, arsenic acts like the metals; in other reactions

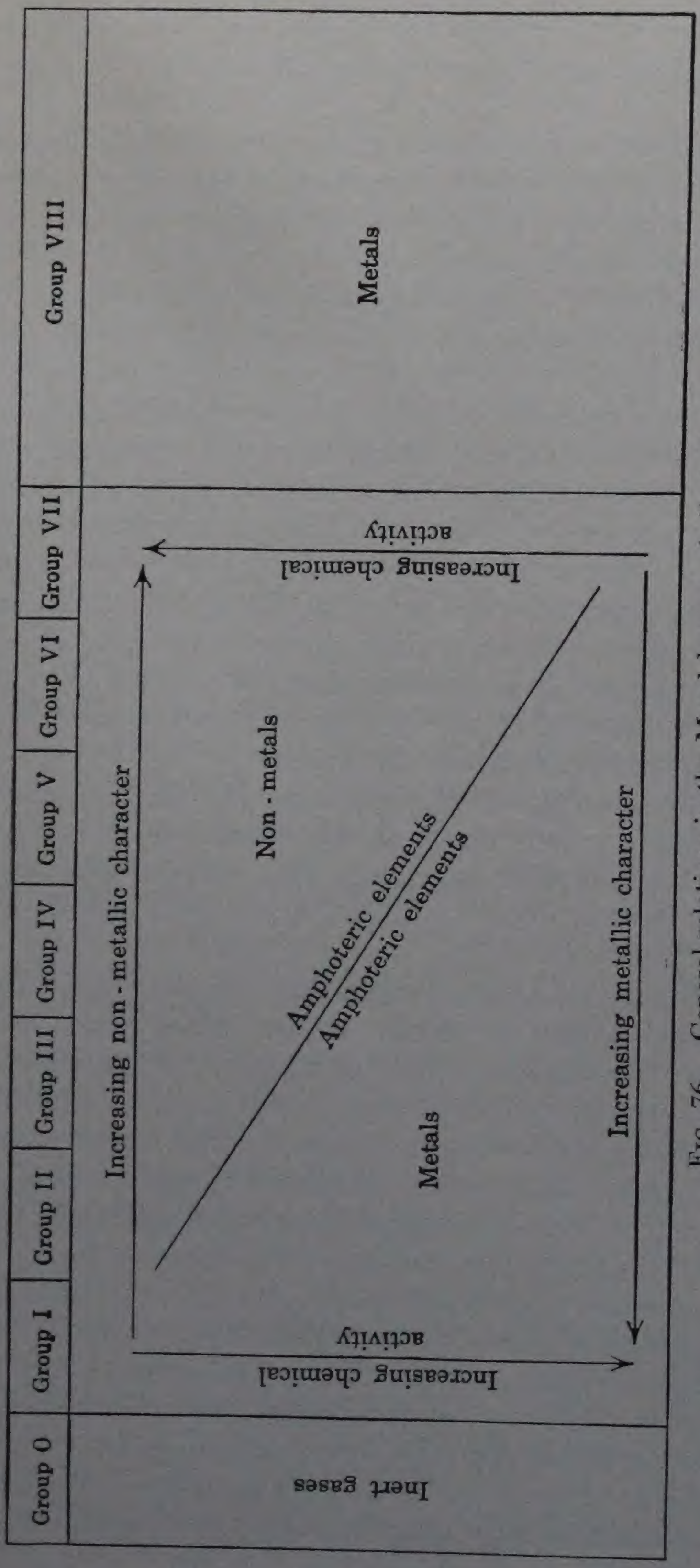

FIG. 76. General relations in the Mendelyeev periodic table.

its behavior is much like that of the typical nonmetals. Elements that exhibit such dual character are sometimes said to be *amphoteric elements.*

Chemical Activity. A fairly good estimate of the relative chemical activity of an element may be gained by considering its position in the periodic table. Aside from the inert gases of Group 0, the chemical activity of the metals *increases* in most cases with increasing atomic number. In Group I, for example, chemical activity increases from lithium to cesium (and presumably to francium, about which relatively little is known). Also in Group I, however, just the reverse trend is exhibited by the elements copper, silver, and gold. It should also be recognized that the tendency toward increase in chemical activity with increase in atomic number becomes less pronounced in each succeeding vertical group as one proceeds from Group I toward the center of the table.

Among the nonmetals (and excluding Group VIII) chemical activity in general *decreases* with increase in atomic number. Accordingly, the most active nonmetals are found in the upper right-hand corner of the table. Again, this trend becomes less marked as one proceeds from Group VII toward the center of the table.

Some of these general relationships are shown diagrammatically in Fig. 76. These trends are best understood if one visualizes this diagram as being superimposed upon the periodic table (Fig. 75).

16.3. Horizontal Periods

Distinct trends in both chemical and physical properties become apparent upon study of the elements of the second period, which begins with the inert gas helium. The next element, lithium, is decidedly metallic in character. Beryllium, in Group II, is predominantly metallic although less so than lithium, but nevertheless possesses a sufficient measure of nonmetallic character to warrant its classification as a metalloid. Boron in Group III is the first element in this period which exhibits a predominance of nonmetallic properties. These nonmetallic characteristics are still more marked in the case of carbon in Group IV and are exhibited in increasing degree in the succeeding elements, nitrogen, oxygen, and fluorine; in fact, fluorine is the most nonmetallic element known. By reference to Fig. 17 it is seen that the sequence of elements from lithium to fluorine involves the quite regular addition of electrons to the second shell. A similar regularity in the electronic development of the third shell is seen to occur from

sodium to chlorine in the third period. This regularity is consistent with the progressive trend from metallic to nonmetallic properties.

In the third period, the first member is the inert gas neon. In this period, sodium is a typical metal, magnesium is somewhat less metallic than sodium, and aluminum is a typical metalloid. Nonmetallic character is first encountered in pronounced degree in the element silicon, and the remainder of the elements in this period become increasingly nonmetallic from silicon to chlorine. It should be recognized at this point that nonmetallic character appears later in the third period than in the second. This tendency becomes more marked in each of the succeeding horizontal periods, a fact which is reflected in the slope of the diagonal line in Fig. 75. Thus, the first predominantly nonmetallic elements in the fourth period are the Group V elements, vanadium and arsenic.

The fourth and fifth periods (long periods) consist of 18 elements each, of which 8 are "normal" elements (like those of the second and third periods) and the remaining 10 are called *transitional elements*. The sixth period consists of 8 normal elements, 10 transitional elements, and 14 *rare-earth elements*, or a total of 32. The seventh period is not fully developed, but it too appears to include a second series of rare-earth elements. Although these long periods involve complexities in structure that are not encountered in the first three periods, the same kinds of regularities and trends are found. Throughout each of the horizontal periods, definite gradations in both chemical and physical properties are encountered.

16.4. Vertical Groups

From the standpoint of simplification of study, a close examination of the relationships exhibited by the elements in any given group proves to be most helpful. The problem may be simplified at the outset by excluding from consideration the inert gases, the transitional metals of Group VIII, and the rare-earth elements. Of the remaining seven groups, each consists of a "main family" and a subgroup. Each main family consists of normal elements, while the subgroups consist of transitional elements. The relationships between the elements in a vertical group can be appreciated best in terms of specific cases. However, before considering Groups I, IV, and VII as typical examples, it is worth while to recall the structural similarity exhibited by the atoms of the elements consigned to each vertical group. From Fig. 17 it is apparent that in any vertical group the total number of electrons

in the outermost shell is the same for all of the elements involved. Thus, in Group II, Be and Mg both have 2 electrons in the outermost shell, and this similarity in structure is responsible for the chemical similarity exhibited by these two elements. However, Be and Mg are not identical, and one would not expect them to be so, for the reason that the Mg atom has, between its outermost shell and its nucleus, a completed shell of 8 electrons not present in the Be atom. Furthermore, the nucleus of the Mg atom is heavier than that of the Be atom, and consequently differences in physical properties are both expected and observed. Also from Fig. 17 it is seen that this same gross structural similarity extends to Ca; diagrams for the structures of the Sr, Ba, and Ra atoms simply constitute an extension. What has been said of Group II applies also in the case of the other vertical groups.

Group I. The main family of Group I consists of the *alkali metals* Li, Na, K, Rb, Cs, and Fr. Because Fr is one of the most recently discovered elements, relatively little is known about either its chemical or physical properties; consequently, it is largely disregarded in the remainder of this discussion. With increasing atomic number, the physical properties of these very metallic elements exhibit surprisingly regular trends. All these metals are solids at ordinary temperatures but are of varying hardness. Thus, lithium has the greatest hardness, sodium is next in hardness, etc. The regularity in the trend of melting temperatures is shown by the data in Table 21. The solubilities (in water) of the compounds of these elements show regular trends; in general, solubility decreases with increase in the atomic number of the alkali metal. Thus, one would expect that RbCl would be less soluble in water than KCl, and such is the case.

TABLE 21

MELTING TEMPERATURES OF THE ALKALI METALS

Alkali metal	Atomic number	Melting temperature, °C.
Li	3	186
Na	11	97.5
K	19	62.3
Rb	37	38.5
Cs	55	28.5
Fr	87	?

Chemical properties also vary more or less regularly throughout each main family. In Group I, chemical activity increases from lithium to cesium, as evidenced, for example, by increasing rates of

reaction with water, oxygen, etc. If an element in a given group forms a certain type of compound, it may be anticipated that the other elements in the group form compounds having similar formulas and properties. For example, lithium combines with oxygen to form the compound (oxide) Li_2O and with hydrogen to form the compound (hydride) LiH. Accordingly, each element in the main family of Group I may be expected to, and does, form similar compounds. Since the alkali metals are base-forming elements, the oxides of the type M_2O dissolve in water to form bases, *e.g.*,

$$Na_2O + H_2O \rightarrow 2NaOH$$

$$Cs_2O + H_2O \rightarrow 2CsOH$$

The basic strengths of the resulting solutions (at equivalent concentrations) increase regularly from Li to Cs; hence CsOH is a stronger base than RbOH, which in turn is a stronger base than KOH, etc.

Although the properties of the elements in the subgroup (Cu, Ag, Au) are in many respects quite different from those of the main-family elements, a sufficient number of similarities is found to justify the allocation of these elements to Group I. On the other hand, the three transitional elements, Cu, Ag, and Au, show marked similarities and trends among themselves and also in relation to the other transitional elements.

Group IV. The fourth periodic group is made up of a main family consisting of C, Si, Ge, Sn, and Pb together with a subgroup containing the three transitional elements Ti, Zr, and Hf. In the main family, C and Si are nonmetallic, Ge (and to a lesser extent Sn) is a metalloid, and Pb is predominantly metallic. Within the subgroup, both Ti and Zr are metalloids. In general, the same sorts of trends in chemical and physical properties are exhibited by Group IV elements as were pointed out in connection with Group I. An important difference, however, lies in the fact that although Group I consists entirely of metals, the entire transition from nonmetallic to metallic character is encountered in Group IV. Another important distinction lies in the fact that, in Group IV, the elements of the subgroup show many more similarities to (and fewer differences from) the elements of the main family than is the case in Group I. In general, Groups I and VII represent extremes with respect to lack of main-family–subgroup similarities, but similarity becomes progressively more marked as one proceeds from either Group I or VII toward Group IV.

Group VII. The halogen family, consisting of F, Cl, Br, I, and the less well known element astatine, At, makes up the main family of

Group VII, while the transitional elements Mn, Tc, and Re constitute the subgroup. As is the case in Group I, the subgroup elements in Group VII exhibit surprisingly few similarities to the elements of the main family.

Perhaps in no other instance are regularities in the trends of behavior and properties illustrated better than by the halogen family. This statement is borne out by an inspection of Table 22, in which are given certain data relating to these nonmetals and their compounds with hydrogen. Within this family, metallic character increases regularly

TABLE 22

PROPERTIES OF ELEMENTS OF THE HALOGEN FAMILY

Property	F	Cl	Br	I
Physical state	Gas	Gas	Liquid	Solid
Color	Colorless	Yellow-green	Brown	Purple
Boiling temp., °C. at 1 atm.	−187°	−33.6°	61.1°	Sublimes
Heat of formation of HX*	+128,000	+44,120	+17,300	−11,820
Stability of HX*	Very stable	Stable	Fairly stable	Unstable
Solubility of HX* in 100 g. H_2O at 25°C	35.3 g.	42.0 g.	49.0 g.	57.0 g.

* Where X represents an element of the halogen family.

from the very nonmetallic fluorine to iodine and astatine, both of which exhibit some decidedly metallic properties. The trend in chemical activity (in the sense of tendency toward gain of electrons) is in the opposite direction, *i.e.*, from the *relatively* inactive astatine to the extremely active fluorine. Thus, chlorine is more active than bromine and is therefore capable of displacing bromine from its compounds. If, for example, an aqueous solution of sodium bromide is treated with gaseous chlorine, a reaction of the following type ensues:

$$2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$$

16.5. Introductory Elements

Since, with one exception, the elements of the second period stand as the first elements in their respective groups, one might be led to assume that the chemical and physical characteristics of these elements might serve as a valid basis for the prediction of the properties of the other elements in each group. Such, however, is not the case. The so-called *introductory elements* exhibit many properties that are abnormal in comparison with those of the other members of their groups. For example, although each introductory element resembles

the corresponding third-period element, it also usually has some properties in common with the third-period element in the next group. Thus, although Li and Na are very similar, Li also resembles Mg in many respects. Similarly, Be resembles both Mg and Al, B has properties in common with both Al and Si, etc. Although these and other unusual characteristics of the introductory elements have been recognized for a long time, a simple and satisfactory explanation for this kind of behavior is not available.

Since a knowledge of the properties of *at least* two elements is necessary in order to establish the trend within a given group and since an introductory element should not be one of these, it is logical to choose the elements in the third and fourth periods. Thus, one would be led to study the elements S and Se in Group VI. If it were found, for example, that Se is more metallic than S, then one would be led to predict (and correctly so) that Te should be more metallic than Se, and that O should be the least metallic element in the main family of Group VI.

16.6. Modified Forms of the Periodic Arrangement

Many modifications of the Mendelyeev classification have been proposed as the result of efforts to clarify relationships not made clear by the Mendelyeev arrangement. These tables have appeared in almost every conceivable form, including numerous three-dimensional models. Although all of these efforts have served useful purposes, it is usually found that modifications designed to clarify certain specific relationships frequently have the disadvantage of obscuring other relationships which are portrayed adequately by the Mendelyeev table. The only modification that need be included here is the periodic table shown in Fig. 77, which has the distinct advantage of a more adequate representation of the interrelationship of the transitional elements. It should be noted that in Fig. 77 the rare-earth series are omitted and that the atomic-weight values included are approximate rather than exact.

16.7. Transitional Elements

The sometimes striking lack of similarity between the elements of a main family and its subgroup has already been indicated. In Group VI, for example, the subgroup consisting of the transitional elements Cr, Mo, and W shows certain marked resemblances to the main family (O, S, Se, Te, and Po), and these resemblances imply that all eight of these elements must have 6 electrons in their outermost shells.

Groups	Ia	IIa	IIIa	IVa	Va	VIa	VIIa	VIII			Ib	IIb	IIIb	IVb	Vb	VIb	VIIb	0	Electron-shell arrangement
At. no.	1																	2	
At. wt.	H 1.008																	He 4	2
At. no.	3	4	5											6	7	8	9	10	
At. wt.	Li 6.9	Be 9	B 10.8											C 12	N 14	O 16	F 19	Ne 20.2	2-8
At. no.	11	12	13											14	15	16	17	18	
At. wt.	Na 23	Mg 24.3	Al 27											Si 28	P 31	S 32	Cl 35.5	A 39.9	2-8-8
At. no.	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
At. wt.	K 39.1	Ca 40	Sc 45.1	Ti 47.9	V 51	Cr 52	Mn 54.9	Fe 55.8	Co 58.9	Ni 58.7	Cu 63.5	Zn 65.4	Ga 69.7	Ge 72.6	As 74.9	Se 79	Br 79.9	Kr 83.7	2-8-18-8
At. no.	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
At. wt.	Rb 85.5	Sr 87.6	Y 88.9	Zr 91.2	Nb 92.9	Mo 96.0	Tc 99	Ru 101.7	Rh 102.9	Pd 106.7	Ag 107.9	Cd 112.4	In 114.8	Sn 118.7	Sb 121.8	Te 127.6	I 126.9	Xe 131.3	2-8-18-18-8
At. no.	55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
At wt.	Cs 132.9	Ba 137.4	La 138.9	Hf 178.6	Ta 180.9	W 184	Re 186.3	Os 190.2	Ir 193.1	Pt 195.2	Au 197.2	Hg 200.6	Tl 204.4	Pb 207.2	Bi 209	Po 210	At 210	Rn 222	2-8-18-32-18-8
At. no.	87	88	89																
At. wt.	Fr 223	Ra 226	Ac 227																

FIG. 77. An improved form of the periodic table (rare-earth series omitted).

On the other hand, the differences that become apparent when one compares the properties of the subgroup elements with those of the main-family elements are the result of a property possessed by all transitional elements, *i.e.*, in the atoms of all transitional elements, the two outermost shells are incomplete or imperfect. It is not surprising that these elements should exhibit some properties not found among main-family elements, which have only one incomplete shell.

All of the elements of Group VIII are transitional elements which show trends in properties similar to the gradations found in any other group. Thus, Fe, Ru, and Os constitute a triad of structurally related elements; consequently, they are similar in chemical and physical properties. The relationship between Group VIII elements and the other transitional elements is shown best by a periodic table of the type given in Fig. 77.

16.8. Rare-earth Elements

The 14 elements corresponding to atomic numbers 58 to 71 inclusive are usually omitted from the main body of the periodic table and listed separately at the bottom, as in Fig. 75. These are known as *rare-earth elements*, and the particular series referred to above is commonly known as the "lanthanide series" for the reason that the series immediately follows the element lanthanum (atomic number 57). Also, the chemical and physical properties of these 14 elements are closely allied to the corresponding properties of La. The rare-earth elements are typified by their striking chemical similarity. The properties of these elements are so much alike that their separation from one another can be accomplished readily only through the use of specially developed methods. In their compounds, the rare-earth elements most commonly exhibit an oxidation number of three, and it is under this condition that they show an especial stability that is characteristic of the group as a whole. These elements differ in structure from all other types in that their atoms have three incomplete or imperfect shells.

Evidence that has become available only within the past few years indicates that a second series of rare-earth elements begins somewhere in the seventh period. By analogy with the sixth period (and for other reasons also), it is logical to assume that this series would begin with the element thorium (atomic number 90), and there is considerable evidence in support of this view. There should be 14 elements in this rare-earth series also, but only 9 of these are known, *i.e.*, elements 90 to 98 inclusive. These nine elements show properties closely analogous to the lanthanide series but differ, for example, in that they exhibit

greater variation in oxidation states in their respective compounds. Again by analogy, this presently incomplete series of rare-earth elements is known as the "actinide series."

It is an interesting and significant fact that most good catalysts are found among the elements having two or more incomplete shells, *i.e.*, the transitional or rare-earth elements or their compounds.

16.9. Synthetic Elements

It is only in recent years that the periodic table has been complete in the sense that elements corresponding to all of the atomic numbers have come to be known. Several elements unknown in Mendelyeev's time—but predicted by him—were discovered in the normal course of events and through the use of more or less conventional experimental methods. By 1939, however, the elements of atomic numbers 43, 61, 85, 87, and all those of atomic number greater than 92 (*i.e.*, 93, 94, 95, 96, 97, and 98) were still unknown.

The bulk of the presently available knowledge concerning 43, technetium (Tc); 61, promethium (Pm); 85, astatine (At); 87, francium (Fr); 93, neptunium (Np); 94, plutonium (Pu); 95, americium (Am); 96, curium (Cm); 97, berkelium (Bk); and 98, californium (Cf) has come almost entirely as the result of discovery of methods whereby elements may be synthesized in the laboratory. One need no longer depend exclusively upon the occurrence of an element in nature; in fact there is still no evidence that 43, 61, 95, 96, 97, or 98 exists in nature at all. Also, 85, 87, 93, and 94 exist in nature in quantities so minute that their isolation from naturally occurring minerals would be either extremely difficult or entirely impractical.

Because the synthesis of elements requires alteration in the nucleus of the atom, chemical changes of a type not heretofore encountered are involved. These changes fall within the domain of "nuclear chemistry," which is the subject of Chap. 30. Study of this chapter also serves to acquaint the student with the methods whereby isotopes of all of the elements have been produced in the laboratory.

GENERAL EXERCISES

1. Into what three broad classes may all the elements be grouped and where are these classes located in the periodic table?
2. Exactly what is meant when one refers to a periodic relationship? State the periodic law.
3. What is the essential difference between the nature of the relationships shown within each horizontal period and those shown within each vertical group?
4. What generalization may be made with regard to the extent to which the

elements in a subgroup may be expected to resemble the elements in the main family of the same group?

5. On the basis of their positions in the periodic table, make predictions regarding the following properties of the elements At and Fr: (*a*) atomic weight, (*b*) chemical activity, (*c*) physical state, (*d*) degree of metallic character, (*e*) chemical character of the binary hydrogen and oxygen compounds, (*f*) stability of the binary hydrogen and oxygen compounds.

6. Given the information that sulfur forms acids having the formulas H_2SO_3 and H_2SO_4, write the formulas for the acids (and for their anhydrides) which one might expect to be formed by the elements Se and Te. Write appropriate names for each of these compounds.

7. Through use of the data given in Table 21, predict the melting temperature of the element francium.

8. If the formula for hydrogen chloride is HCl, write the formulas and names for the chlorides of all of the elements of Group I.

9. If the formula for magnesium bromide is $MgBr_2$, write the formulas and names for the bromides of all of the elements of Group II.

10. From their positions in the periodic table, and in consideration of the structures of the atoms involved, write formulas and names for an oxide of each of the following elements: (*a*) Si, (*b*) Cl, (*c*) Ba, (*d*) Ga, (*e*) Kr, (*f*) Cu.

11. If the electrons in the various shells are subject to the attractive forces of the positively charged nucleus, offer explanations for the following facts: (*a*) In the main family of Group I, chemical activity *increases* with increase in atomic number. (*b*) In the main family of Group VII, chemical activity *decreases* with increase in atomic number.

12. Into what four groups may the elements be divided in terms of the number of incomplete or imperfect electron shells?

SUGGESTED READING

Journal of Chemical Education

Kraus, The Amphoteric Elements, **8,** 2126 (1931).
Martin, Another Periodic Table, **18,** 526 (1941).
Payne, A Periodic System of the Elements, **15,** 180 (1938).
Luder, Electron Configuration as the Basis of the Periodic Table, **20,** 21 (1943).
Babor, A Periodic Table Based on Atomic Number and Electron Configuration, **21,** 25 (1944).
Emerson, A New Spiral Form of the Periodic Table, **21,** 111 (1944).
Wagner and Booth, A New Periodic Table, **22,** 128 (1945).
Hopkins, Chemistry of the Rare Earth Group, **13,** 224 (1936).
Pearce and Selwood, Anomalous Valences of the Rare Earths, **13,** 224 (1936).

Book

Weeks, "Discovery of the Elements," Journal of Chemical Education, Easton, Pa., 1945.

CHAPTER 17

TYPES OF CHEMICAL REACTIONS

Throughout the preceding chapters, numerous examples of chemical changes have been cited for the purpose of illustrating principles, characteristic types of chemical behavior, etc., and equations for these reactions have been written, usually by inspection. In all, however, only a relatively few reactions have been studied in detail. Before attempting any further study of individual chemical changes, it seems worth while to inquire into the manner in which different reactions are related one to the other. Just as classification of the chemical elements leads to simplification of study, so perhaps the various types of chemical reactions may be correlated to advantage.

OXIDATION-REDUCTION REACTIONS

In terms of their historical origin, the terms *oxidation* and *reduction* are related to certain practices in the chemical industries, and from a more modern point of view these terms are not entirely satisfactory; The term oxidation implies or at least suggests the element oxygen. however, oxygen need not be involved in reactions of this type. Despite the fact that these two terms are somewhat misleading, they have become so firmly entrenched in the language of chemistry that they will undoubtedly continue to be used indefinitely.[1]

17.1. Characteristics of Oxidation-Reduction Reactions

The terms oxidation and reduction are defined in Sec. 4.8, where the interrelationship and interdependence of these two processes are given particular emphasis. It is recommended that the student review thoroughly Sec. 4.8 before proceeding with the study of the present chapter.

[1] In efforts to find more suitable designations for reactions of this type, numerous alternatives have been suggested. Thus, oxidation-reduction reactions are sometimes referred to as *electron-change reactions*, *electronic reactions*, *electron-exchange reactions*, *redox reactions*, etc. It has also been suggested that the terms *de-electronation* and *electronation* be substituted for the terms oxidation and reduction, respectively. Although some merit may be involved in each of these alternatives, none has met with general acceptance.

Chemical changes classified as oxidation-reduction reactions may differ considerably so far as the nature of the reactants and products is concerned and yet have much in common with respect to the fundamental character of the changes that are involved. By definition it is apparent that in every oxidation-reduction reaction, one or more elements must undergo a change in valence. The elements that experience the change in valence may be in combination in the form of ionic, covalent, or intermediate types of compounds. Where covalent compounds are involved, the actual loss and gain of electrons may be more apparent than real. In the writing of equations for oxidation-reduction reactions, it is consequently unnecessary to attempt to distinguish between ionic and covalent species; rather, it is sufficient merely to indicate the appropriate states of oxidation in terms of oxidation numbers.

17.2. Oxidation States

Because the element sulfur commonly exhibits variable valence in both ionic and covalent types of combination, this element is used to illustrate states of oxidation. It may be recalled that sulfur is in periodic Group VI and that the neutral sulfur atom (designated[1] S^0) has 6 electrons in its outermost shell. In terms of the closest approach to an inert-gas structure, the neutral sulfur atom tends to gain 2 electrons (*i.e.*, reduction) and thus achieve a lower state of oxidation.[2] It must be recognized however that this gain of 2 electrons might occur in two steps,

$$S^0 + 1e^- \rightarrow S^-$$

$$S^- + 1e^- \rightarrow S^{2-}$$

and that the sequence of changes,

$$S^0 \rightarrow S^- \rightarrow S^{2-}$$

corresponds to progressively lower states of oxidation. Since, having gained 2 electrons, the sulfur atom has achieved its nearest approach to an inert-gas configuration, the sulfur atom cannot be reduced further, *i.e.*, the dinegative sulfide ion represents the lowest possible oxidation state of sulfur.

[1] Whether or not the zero superscript is included, any substance in the elemental state is understood to be in the zero oxidation state.

[2] A lower state of oxidation of course corresponds to a higher state of reduction. Although all of these changes could be equally well designated in terms of reduction states, this terminology is only infrequently used.

If, now, one should start with sulfur in its lowest oxidation state (S^{2-}), by progressive loss of electrons (oxidation) the sulfur may be converted to progressively higher oxidation states. For example, the sulfide ion might be oxidized to elemental sulfur,

$$S^{2-} - 2e^- \rightarrow S^0$$

and it should be apparent that S^0 represents a higher oxidation state than S^{2-} since loss of electrons is involved in the indicated reaction.

Since the neutral sulfur atom has 6 electrons in its outermost shell, presumably these electrons also might be lost. In any event, whether they are actually lost or not, the sulfur atom participates in chemical changes that can be conveniently represented as involving oxidation. Thus, sulfur may be oxidized to sulfur dioxide, and because the apparent oxidation number (*i.e.*, valence) of S in SO_2 is 4+, the essential change is represented by

$$S^0 - 4e^- \rightarrow S^{4+}$$

If the sulfur atom loses four electrons, these must be gained by another reactant, in this case oxygen. Each of the 2 atoms of oxygen (also a Group VI element) in an oxygen molecule may gain 2 electrons in a reduction reaction in which the oxidation state of oxygen changes from 0 to 2−,

$$O_2^0 + 4e^- \rightarrow 2O^{2-}$$

Thus one may write for (*a*) the oxidation step, and (*b*) the reduction step

$$(a) \quad S^0 - 4e^- \rightarrow S^{4+}$$

$$(b) \quad O_2^0 + 4e^- \rightarrow 2O^{2-}$$

from which it is seen that the requirement that the number of electrons involved in each step must be the same is met. Hence by canceling and adding, one obtains the final complete equation

$$(c) \quad S^0 + O_2^0 \rightarrow SO_2$$

Suppose further that one wished to represent the oxidation of sulfur to its highest oxidation state, S^{6+}, which requires the loss of all 6 electrons in the outermost shell. This could be accomplished by oxidizing sulfide ion (loss of $8e^-$), elemental sulfur (loss of $6e^-$), sulfur in sulfur dioxide (loss of $2e^-$), or in fact the oxidation of sulfur in any oxidation state lower than 6^+. For the oxidation of sulfur dioxide to sulfur

trioxide, for example, one would write,

$$\begin{array}{ll} (a) & S^{4+} - 2e^- \rightarrow S^{6+} \\ (b) & O^0 + 2e^- \rightarrow O^{2-} \\ \hline (c) & S^{4+} + O^0 \rightarrow S^{6+} + O^{2-} \end{array}$$

but (*c*) does not represent the initial or final conditions of combination; neither does it take into account that the oxygen which reacts is supplied in the form of O_2 molecules. Consequently, step (*b*) must be multiplied by 2, and the same must be done in step (*a*) in order that the number of electrons may remain the same in the two equations,

$$\begin{array}{ll} (a) & 2S^{4+} - 4e^- \rightarrow 2S^{6+} \\ (b) & O_2^0 + 4e^- \rightarrow 2O^{2-} \\ \hline (c) & 2S^{4+} + O_2^0 \rightarrow 2S^{6+} + 2O^{2-} \end{array}$$

Step (*c*) now needs to be modified further to show that the S^{4+} was used in the form of SO_2, and that the product S^{6+} is in the form of SO_3, hence,

$$(d) \qquad 2SO_2 + O_2 \rightarrow 2SO_3$$

These are, to be sure, relatively simple cases in which the equations could easily be written by inspection. The purpose of these examples is simply to illustrate a systematic method whereby one may write equations for much more complicated reactions and at the same time represent the essential steps in the processes of loss and gain of electrons.

Attention is also called to the fact that the numbers ("oxidation numbers") written to show the oxidation states (apparent valences) of the essential reactants and products are included in all cases except that in which the oxidation number is one. This practice is continued in the following pages, and the oxidation reaction is written first in all cases.

With these ideas as a background, it is now possible to review profitably some of the reactions studied previously, to attempt to gain a better insight into the fundamental changes involved, and to show why they must be classified as oxidation reduction reactions.

17.3. Reactions Involving Direct Union of Elements

Several reactions of this type have already been discussed, particularly in connection with the study of oxygen (Sec. 5.9). As an additional example, consider the formation of bismuth bromide by the direct union of bismuth and bromine.

$$2Bi + 3Br_2 \rightarrow 2BiBr_3$$

This equation represents adequately the over-all change involved and can be balanced readily by trial and error if by no other means. However, such an equation fails to show what occurs during the union of the elements concerned. In this reaction the bismuth atom apparently loses its 3 outermost electrons and, by definition, is thereby oxidized. Accordingly, the oxidation reaction may be represented as

$$(a) \qquad Bi - 3e^- \rightarrow Bi^{3+}$$

Each bromine atom in the bromine molecule is capable of gaining 1 electron; hence the reduction may be represented as

$$(b) \qquad Br_2 + 2e^- \rightarrow 2Br^-$$

However, it is readily seen that the number of electrons lost in (*a*) is different from the number gained in (*b*). This may be remedied by multiplying Eq. (*a*) by 2 and multiplying Eq. (*b*) by 3, thus,

$$(a) \qquad 2Bi - 6e^- \rightarrow 2Bi^{3+}$$

$$(b) \qquad 3Br_2 + 6e^- \rightarrow 6Br^-$$

Adding Eqs. (*a*) and (*b*),

$$(c) \qquad 2Bi + 3Br_2 \rightarrow 2BiBr_3$$

This method of representing oxidation-reduction reactions may be applied in a similar fashion to other reactions involving the direct union of elements (see General Exercises).

17.4. Displacement Reactions

In a manner comparable to that illustrated above, the equations for reactions previously cited in connection with the displacement of hydrogen from acids, water, and bases (Sec. 9.1) may be rewritten as typical oxidation-reduction changes. Reactions involving displacement of elements other than hydrogen are treated similarly.

Displacement of Hydrogen from Acids. The reaction between zinc and sulfuric acid,

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

in which zinc is oxidized and hydrogen is reduced, may be written in the form,

$$(a) \qquad Zn - 2e^- \rightarrow Zn^{2+}$$

$$(b) \qquad 2H^+ + 2e^- \rightarrow H_2$$

$$(c) \qquad Zn + 2H^+ \rightarrow Zn^{2+} + H_2$$

In order to show (in addition to the essential oxidation and reduction steps) the origin of the hydrogen ions reduced in step (*b*) and the ultimate fate of the Zn^{2+}, it is necessary to write a fourth equation,

$$(d) \qquad Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

Displacement of Hydrogen from Water. The oxidation of magnesium and the reduction of hydrogen ions in the reaction between magnesium and water,

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$$

may be represented as an oxidation-reduction reaction as follows:

$$\begin{array}{ll} (a) & Mg - 2e^- \rightarrow Mg^{2+} \\ (b) & 2H^+ + 2e^- \rightarrow H_2 \\ \hline (c) & Mg + 2H^+ \rightarrow Mg^{2+} + H_2 \\ (d) & Mg + 2HOH \rightarrow Mg(OH)_2 + H_2 \end{array}$$

In this reaction, hydrogen is the oxidizing agent and magnesium is the reducing agent.

Displacement of Hydrogen from Bases. When represented as an oxidation-reduction reaction, the interaction of aluminum and sodium hydroxide,

$$2Al + 6NaOH \rightarrow 2Na_3AlO_3 + 3H_2$$

becomes

$$\begin{array}{ll} (a) & 2Al - 6e^- \rightarrow 2Al^{3+} \\ (b) & 6H^+ + 6e^- \rightarrow 3H_2 \\ \hline (c) & 2Al + 6H^+ \rightarrow 2Al^{3+} + 3H_2 \\ (d) & 2Al + 6NaOH \rightarrow 2Na_3AlO_3 + 3H_2 \end{array}$$

In the compound Na_3AlO_3, aluminum has an apparent valence of 3+, because each of the more negative oxygen atoms has a valence of 2− ($3 \times 2- = 6-$), and each of the more positive sodium atoms has a valence of 1+ ($3 \times 1+ = 3+$). Accordingly, the valence of Al must be 3+ since the molecule must be electrically neutral.

17.5. Decomposition of Compounds

A very wide variety of reactions involving the decomposition of compounds must also be classified as oxidation-reduction changes. The products of such reactions may be the constituent elements, other compounds, or elements and compounds. The decomposition of

potassium chlorate by means of heat (Sec. 3.3),

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

serves as a suitable illustration. Here, the apparent valence of Cl in $KClO_3$ is 5+, while in KCl the valence of Cl is 1−. Hence, in this reaction, chlorine gains electrons (is reduced). By loss of electrons, oxygen is oxidized from O^{2-} to elemental oxygen (oxidation number = 0). Consequently, oxygen is the reducing agent and chlorine is the oxidizing agent.

$$\begin{array}{ll} (a) & 6O^{2-} - 12e^- \rightarrow 3O_2 \\ (b) & 2Cl^{5+} + 12e^- \rightarrow 2Cl^- \\ \hline (c) & 2Cl^{5+} + 6O^{2-} \rightarrow 2Cl^- + 3O_2 \\ (d) & 2KClO_3 \rightarrow 2KCl + 3O_2 \end{array}$$

17.6. Factors That Influence the Extent of Oxidation and Reduction

If it is true that an element in a particular state of oxidation may either gain or lose one or more electrons and thus pass into successively lower or higher states of oxidation, there arises the question of what factors influence the extent of oxidation and reduction, and of the means whereby one may exercise control over such reactions. If, upon bringing together an oxidizing agent and a reducing agent, two or more reactions are possible, the predominant reaction is that which proceeds at the greatest rate under the particular experimental conditions employed. Consequently, since the relative rates of competitive reactions are involved, oxidation-reduction reactions are subject to influence by the same factors that have bearing upon the rates of chemical reactions in general, *viz.*, temperature, concentration, and catalysis. In addition, the extent of oxidation and reduction is governed largely by the inherent characteristics of the particular oxidizing and reducing agents concerned. This fact may be illustrated best by consideration of a specific case.

Suppose that a metal M is to be oxidized to M^+ by its reaction with concentrated sulfuric acid at room temperature. In H_2SO_4, sulfur has an apparent oxidation number of 6+, and it is recognized that this S^{6+} might be reduced to S^{5+}, S^{4+}, S^{3+}, S^{2+}, S^+, S^0, S^-, or S^{2-}. Of these possible lower oxidation states, that which is formed (or that which predominates, if a mixture of products is realized) is determined by the relative effectiveness of M as a reducing agent. Since the role of reducing agents is that of losing the electrons needed for the reduction reaction, the effectiveness or "strength" of reducing agents is therefore

dependent upon their inherent tendencies toward loss of electrons. As is shown in Chap. 21, and more specifically in Table 24, these tendencies may be expressed in quantitative terms, and these data serve as a basis for predictions relative not only to the occurrence of oxidation-reduction reactions but also to the extent to which such processes occur. If, for example, metal M has a great tendency toward loss of electrons, it would be expected that S^{6+} would be reduced to a relatively low oxidation state, perhaps to elemental sulfur or to sulfide ion. Less extensive reduction would be anticipated if one should use a metal having a relatively lesser tendency toward loss of electrons. Information of the type assembled in Table 24 permits one to select oxidizing and reducing agents in accordance with the reaction products desired.

17.7. Some Common Oxidation-Reduction Reactions

A type of oxidation-reduction reaction commonly encountered is that which occurs when a metal is dissolved in an oxidizing acid such as nitric acid. When, for example, copper is dissolved in *concentrated* nitric acid, the N^{5+} in HNO_3 is reduced only to N^{4+}, owing to the fact that copper is a very weak reducing agent (see Table 24). The corresponding equations are

$$(a) \quad Cu - 2e^- \rightarrow Cu^{2+}$$
$$(b) \quad 2N^{5+} + 2e^- \rightarrow 2N^{4+}$$
$$(c) \quad Cu + 2N^{5+} \rightarrow Cu^{2+} + 2N^{4+}$$
$$(d) \quad Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

It should be noted that the number of moles of HNO_3 included in step (d) is 4 rather than the 2 moles implied by step (b). This is necessary because two nitrate ions are required for combination with the Cu^{2+} ion formed in step (a).

If, on the other hand, one should use lead as the reducing agent, its greater effectiveness as an electron donor permits reduction of N^{5+} in concentrated HNO_3 to N^{3+}, or in other words, reduction of HNO_3 to HNO_2, thus

$$(a) \quad Pb - 2e^- \rightarrow Pb^{2+}$$
$$(b) \quad N^{5+} + 2e^- \rightarrow N^{3+}$$
$$(c) \quad Pb + N^{5+} \rightarrow Pb^{2+} + N^{3+}$$
$$(d) \quad Pb + 3HNO_3 \rightarrow Pb(NO_3)_2 + HNO_2 + H_2O$$

Use of the still stronger reducing agent zinc results in reduction of

N^{5+} to N^{2+}, *i.e.*, from HNO_3 to NO, in accordance with the following equations:

$$(a) \quad 3Zn - 6e^- \rightarrow 3Zn^{2+}$$
$$(b) \quad 2N^{5+} + 6e^- \rightarrow 2N^{2+}$$
$$(c) \quad 3Zn + 2N^{5+} \rightarrow 3Zn^{2+} + 2N^{2+}$$
$$(d) \quad 3Zn + 8HNO_3 \rightarrow 3Zn(NO_3)_2 + 2NO + 4H_2O$$

Since nitrogen is in Group V in the periodic table, its ultimate reduction to N^{3-} (as in NH_3) should be possible. As shown above, however, use of the relatively strong reducing agent zinc (see Table 24) in reaction with concentrated nitric acid leads to reduction to only the 2+ state. Reduction to still lower oxidation states may be accomplished by using dilute rather than concentrated nitric acid, since the ease of reduction of N^{5+} in HNO_3 increases with decrease in the concentration of the acid. This brings up still another complication, which leads to the conclusion that the situation portrayed by the three preceding sets of equations is not so simple as it might appear. For example, if one adds solid zinc to concentrated nitric acid, the concentration of the acid decreases as the reaction proceeds. Consequently, although NO may be the predominant product of the reaction, other products representing lower oxidation states are to be anticipated depending upon the specific conditions employed.

Many oxidation-reduction changes are employed in the course of laboratory work in qualitative and quantitative analysis. A typical case is that of the reduction of mercuric chloride by means of stannous chloride. If to a solution thought to contain Sn^{2+} one adds mercuric chloride, the latter is reduced to white insoluble[1] mercurous chloride if Sn^{2+} is present.

$$(a) \quad Sn^{2+} - 2e^- \rightarrow Sn^{4+}$$
$$(b) \quad 2Hg^{2+} + 2e^- \rightarrow 2Hg^{+}$$
$$(c) \quad Sn^{2+} + 2Hg^{2+} \rightarrow Sn^{4+} + 2Hg^{+}$$
$$(d) \quad SnCl_2 + 2HgCl_2 \rightarrow SnCl_4 + \underline{Hg_2Cl_2}$$

(Incidentally, the 4+ oxidation state for tin should be anticipated since this element is in Group IV in the periodic table.) Further reaction with stannous chloride results in reduction of the white mercurous

[1] In equation (*d*) the formula for mercurous chloride is underscored to indicate that it is an insoluble product. In the pages that follow, this practice is continued, but only when it is desired particularly to emphasize insolubility.

chloride to black elemental mercury,

$$\begin{array}{ll} (a) & Sn^{2+} - 2e^- \rightarrow Sn^{4+} \\ (b) & 2Hg^{+} + 2e^- \rightarrow 2Hg \\ \hline (c) & Sn^{2+} + 2Hg^{+} \rightarrow Sn^{4+} + 2Hg \\ (d) & SnCl_2 + \underline{Hg_2Cl_2} \rightarrow SnCl_4 + \underline{2Hg} \end{array}$$

and this sequence of changes is so characteristic that it may be used for the identification of either tin or mercury.

Although stannous chloride is most commonly used as a reducing agent, it should be kept in mind that, in the presence of a still stronger reducing agent, stannous chloride would act as an oxidizing agent and could be reduced to elemental tin.

Other oxidation-reduction reactions that have been found useful in chemical analysis include the oxidation of ferrous sulfate by potassium dichromate in the presence of sulfuric acid,

$$\begin{array}{ll} (a) & 6Fe^{2+} - 6e^- \rightarrow 6Fe^{3+} \\ (b) & 2Cr^{6+} + 6e^- \rightarrow 2Cr^{3+} \\ \hline (c) & 6Fe^{2+} + 2Cr^{6+} \rightarrow 6Fe^{3+} + 2Cr^{3+} \\ (d) & 6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 \\ & \qquad + K_2SO_4 + 7H_2O \end{array}$$

the oxidation of hydrogen sulfide by means of potassium permanganate, also in the presence of sulfuric acid,

$$\begin{array}{ll} (a) & 5S^{2-} - 10e^- \rightarrow 5S \\ (b) & 2Mn^{7+} + 10e^- \rightarrow 2Mn^{2+} \\ \hline (c) & 5S^{2-} + 2Mn^{7+} \rightarrow 5S + 2Mn^{2+} \\ (d) & 5H_2S + 2KMnO_4 + 3H_2SO_4 \rightarrow 5S + 2MnSO_4 + K_2SO_4 \\ & \qquad + 8H_2O \end{array}$$

and the oxidation of manganous nitrate to permanganic acid by the use of sodium bismuthate as the oxidizing agent, in the presence of nitric acid,

$$\begin{array}{ll} (a) & 2Mn^{2+} - 10e^- \rightarrow 2Mn^{7+} \\ (b) & 5Bi^{5+} + 10e^- \rightarrow 5Bi^{3+} \\ \hline (c) & 2Mn^{2+} + 5Bi^{5+} \rightarrow 2Mn^{7+} + 5Bi^{2+} \\ (d) & 2Mn(NO_3)_2 + 5NaBiO_3 + 16HNO_3 \rightarrow 2HMnO_4 + 5Bi(NO_3)_3 \\ & \qquad + 5NaNO_3 + 7H_2O \end{array}$$

METATHETICAL REACTIONS

Quite apart from oxidation-reduction reactions that involve changes in oxidation numbers is a class of reactions that may be represented by the general equation,

$$A^+B^- + C^+D^- \rightarrow A^+D^- + C^+B^-$$

wherein no change in valence occurs and the reaction takes place by a process amounting to "double displacement." Such chemical changes are usually called *metathetical reactions*,[1] and the over-all process is termed *metathesis*. In the sections that follow, the discussion of metathetical reactions is largely restricted to those which occur *in dilute solutions at or near room temperature*.

17.8. Neutralization

Reactions between acids and bases are typical metathetical reactions, as may be seen from the comparison,

$$A^+B^- + C^+D^- \rightarrow AD + C^+B^-$$

$$H^+Cl^- + Na^+(OH)^- \rightarrow H(OH) + Na^+Cl^-$$

If a dilute solution of H^+ and Cl^- ions (hydrochloric acid solution) is added to a dilute solution of Na^+ and $(OH)^-$ ions (sodium hydroxide solution), the ensuing reaction produces *molecules* of the slightly ionized weak electrolyte H_2O, by virtue of the union of H^+ and $(OH)^-$ ions, thus,

$$H^+ + (OH)^- \rightarrow H_2O$$

The Na^+ and Cl^- ions, which were already present before the acid and base were mixed, are also present as such after the reaction (formation of H_2O) has gone to completion. *The salt Na^+Cl^- is not actually formed in the reaction.* The ions corresponding to this salt are present in the solution, and, of course, solid crystals of Na^+Cl^- may be obtained by evaporation of the solvent. Thus, the essential change involved in this metathetical neutralization reaction is the formation of water, and this feature is common to all reactions between acids and bases in aqueous solution.

[1] In addition to the use of the term *metathetical*, reactions of this type are variously referred to as *double decomposition reactions*, *ionic reactions*, *change-of-partner reactions*, etc. Since the literal meaning of the term metathetical is *displacement*, this term is perhaps no more suitable than any of the others.

17.9. Reactions between Salts and Acids

The metathetical interaction of salts and acids may be illustrated by the following equation:

$$Ag^+(NO_3)^- + H^+Cl^- \rightarrow \underline{Ag^+Cl^-} + H^+(NO_3)^-$$

In this reaction, Ag^+ and Cl^- ions combine to form *insoluble* silver chloride without any actual change being experienced by the H^+ and $(NO_3)^-$ ions,

$$Ag^+ + Cl^- \rightarrow \underline{Ag^+Cl^-}$$

The insoluble silver chloride may be removed by filtration, and the resulting clear solution would exhibit all the properties of a dilute solution of nitric acid.

17.10. Reactions between Salts and Bases

The reaction between ammonium chloride and barium hydroxide serves as an example of this rather common and useful type of reaction,

$$2(NH_4)^+Cl^- + Ba^{++}(OH)_2^- \rightarrow 2(NH_4)(OH) + Ba^{++}Cl_2^-$$

The essential reaction in this case is the formation of the weak electrolyte NH_4OH,

$$(NH_4)^+ + (OH)^- \rightarrow (NH_4)(OH)$$

Barium and chloride ions are present as such both before and after the occurrence of the above reaction.

If ammonium sulfate were to be used in place of ammonium chloride,

$$(NH_4)_2^+ SO_4^= + Ba^{++}(OH)_2^- \rightarrow 2(NH_4)(OH) + \underline{Ba^{++}(SO_4)^=}$$

all the ions concerned would be involved since

$$(NH_4)^+ + (OH)^- \rightarrow NH_4OH$$

and

$$Ba^{++} + (SO_4)^= \rightarrow \underline{Ba^{++}(SO_4)^=}$$

Thus one pair of ions unites to form a weak electrolyte, and the other pair actually combines to form an insoluble solid. Accordingly, it must be recognized that either one *or more* pairs of ions must combine during the occurrence of a metathetical reaction.

17.11. Reactions between Salts

This type of metathetical reaction may be illustrated by the interaction of silver nitrate and sodium chloride,

$$Ag^+(NO_3)^- + Na^+Cl^- \rightarrow \underline{Ag^+Cl^-} + Na^+(NO_3)^-$$

in which the essential change is the formation of insoluble silver chloride,

$$Ag^+ + Cl^- \rightarrow \underline{Ag^+Cl^-}$$

By comparison with the reaction between silver nitrate and hydrochloric acid solution (Sec. 17.9), it is seen that these two metathetical reactions are fundamentally the same since they both occur for the same reason, *viz.*, the union of silver and chloride ions.

Another example of this type of reaction is that between lead nitrate and potassium acetate,

$$Pb^{++}(NO_3)_2^- + 2K^+(C_2H_3O_2)^- \rightarrow Pb(C_2H_3O_2)_2 + 2K^+(NO_3)^-$$

a reaction that occurs because of the union of lead and acetate ions to form molecules of the slightly ionized weak electrolyte lead acetate.

17.12. Factors Involved in the Occurrence of Metathetical Reactions

The preceding examples are sufficient to show that a metathetical reaction occurs when the concentration of one or more pairs of ions is decreased as a result of the formation of a weak electrolyte or an insoluble substance. It is also of importance not only to recognize that certain metathetical reactions occur, but also to be able to estimate the extent to which such reactions proceed to completion. The chemist is frequently faced with the problem of predicting whether a given metathetical reaction will occur at all and, if so, whether it will proceed to completion.

Consider, for example, the reaction between mercuric nitrate and sodium cyanide,

$$Hg^{++}(NO_3)_2^- + 2Na^+(CN)^- \rightarrow Hg(CN)_2 + 2Na^+(NO_3)^-$$

One would predict that this reaction will occur because the concentration of a pair of ions [Hg^{++} and $(CN)^-$] will be decreased owing to the formation of the weak electrolyte mercuric cyanide. Further, since $Hg(CN)_2$ is a very weak electrolyte, substantially all of the Hg^{++} and $(CN)^-$ ions become tied up in the form of molecules of mercuric cyanide and the reaction proceeds essentially to completion.

Similarly, one would predict that the reaction between copper nitrate and phosphoric acid,

$$3Cu^{++}(NO_3)_2^- + 2H_3(PO_4) \rightarrow \underline{Cu_3^{++}(PO_4)_2^{=}} + 6H^+(NO_3)^-$$

would not only occur but would also go to completion owing to the fact

that copper phosphate is very insoluble and its formation results in a decrease in the concentration of copper and phosphate ions in the solution.

On the other hand, consider the equation for a proposed reaction between magnesium acetate and ammonium chloride.

$$Mg^{++}(C_2H_3O_2)_2^- + 2(NH_4)^+Cl^- \rightarrow Mg^{++}Cl_2^- + 2(NH_4)^+(C_2H_3O_2)^-$$

It may be seen that this reaction does not occur since neither a weak electrolyte nor an insoluble substance is formed. Hence, the total ion concentration is not changed upon bringing together solutions of these two salts.

Accordingly, the problem of deciding whether a given metathetical reaction occurs involves the ability to recognize (*a*) weak electrolytes and (*b*) insoluble substances. Information relative to common acids, bases, and salts that are classified as weak electrolytes has already been provided (Sec. 14.6), and some general rules relating to solubility relationships are outlined in the following section. Once the fact that a metathetical reaction occurs has been established, it must be recognized that the extent to which it proceeds toward completion is dependent upon the properties of the substance whose formation is responsible for the occurrence of the reaction. If a metathetical reaction occurs because of the formation of a weak electrolyte, the weaker the electrolyte the more nearly the reaction proceeds to completion. Similarly, if the formation of an insoluble substance is involved, the more insoluble the substance, the greater the extent of reaction. Hence, it is concluded that "completion" of metathetical reactions is dependent upon the effectiveness of weak-electrolyte or insoluble-product formation in decreasing the concentration of at least one pair of ions.

17.13. Solubilities of Common Acids, Bases, and Salts

Before studying the following generalizations with respect to solubility relationships, the student should review Sec. 10.5.

It must be recognized at the outset that any effort to classify solutes in relation to the extent to which they dissolve in a solvent such as water is likely to be none too successful owing to wide variations in solubility and to difficulties involved in deciding just where to draw a line of demarcation between substances which are to be considered as soluble and those which are to be looked upon as insoluble. Nevertheless, it is possible to set up a few general rules to serve as a practical working basis for the purpose at hand as well as for certain other pur-

poses. The generalizations given relate *only* to solubility in water at room temperature.

Acids. All *common* acids are *soluble* with the exception of silicic acid [$H_2(SiO_3)$] and arsenious acid [$H(AsO_2)$].

Bases. All *common* bases are *insoluble* with the exception of the following:

Ammonium hydroxide (NH_4OH)	extensively soluble
Sodium hydroxide ($NaOH$)	extensively soluble
Potassium hydroxide (KOH)	extensively soluble
Calcium hydroxide [$Ca(OH)_2$]	sparingly soluble
Strontium hydroxide [$Sr(OH)_2$]	sparingly soluble
Barium hydroxide [$Ba(OH)_2$]	sparingly soluble

Salts. All *common* sodium, potassium, and ammonium salts are extensively *soluble*.

All silver salts are *insoluble* except silver fluoride (AgF), silver nitrate [$Ag(NO_3)$], and silver chlorate [$Ag(ClO_3)$]. Silver acetate [$Ag(C_2H_3O_2)$] and silver sulfate [$Ag_2(SO_4)$] are only *sparingly soluble*.

All nitrates, acetates, and chlorates are extensively soluble except silver acetate (see above).

All *normal* sulfates are *soluble* except lead sulfate [$Pb(SO_4)$], strontium sulfate [$Sr(SO_4)$], and barium sulfate [$Ba(SO_4)$], which are *insoluble*, and mercurous sulfate [$Hg_2(SO_4)$] and silver sulfate [$Ag_2(SO_4)$], which are only *sparingly soluble*.

All chlorides are *moderately to extensively soluble* except silver chloride (AgCl) and mercurous chloride (Hg_2Cl_2). Lead chloride ($PbCl_2$) is only slightly soluble.

All *normal* sulfides, carbonates, sulfites, silicates, and phosphates are *insoluble* except those of sodium, potassium, and ammonium.

In general, *acid salts* are *soluble*.

As the student acquires more and more information concerning the specific properties of individual chemical compounds, it is inevitable that numerous exceptions to the foregoing generalizations will be encountered.

GENERAL EXERCISES[1]

1. Define the following terms: (*a*) oxidation, (*b*) oxidizing agent, (*c*) reducing agent, (*d*) metathesis, (*e*) reduction.
2. List the characteristic features of oxidation-reduction reactions.
3. Why must oxidation and reduction reactions always occur simultaneously?
4. What is the most important distinction between oxidation-reduction reactions and metathetical reactions?

[1] Unless otherwise indicated by the instructor, all oxidation-reduction equations required in these exercises are to be written by the method outlined in this chapter.

5. Of the two states of oxidation indicated in each of the following cases, which one represents the higher state of oxidation (*i.e.*, the more highly oxidized form)? (*a*) S^0 or S^-, (*b*) Cu^0 or Cu^{2+}, (*c*) I_2 or I^-, (*d*) Pb^{4+} or Pb, (*e*) Pb^{2+} or Pb^{4+}, (*f*) H_2 or H^+.

6. If each of the following compounds was to be oxidized by means of a suitable oxidizing agent, (*a*) which element would most likely lose electrons, and (*b*) what would be the final state of oxidation of that element? (1) Cu_2Cl_2, (2) KBr, (3) PbO, (4) Na_2S, (5) As_2O_3, (6) $ZnCl_2$.

7. Essentially what is implied when one states that two reducing agents are of different strengths?

8. Write equations for the following oxidation-reduction reactions:

(*a*) The direct union of (1) lead and sulfur, (2) magnesium and oxygen, (3) sulfur dioxide and oxygen, (4) carbon and sulfur, (5) hydrogen and oxygen.

(*b*) The decomposition (by application of heat) of (1) potassium nitrate, (2) mercuric oxide, (3) lead dioxide, (4) manganese dioxide.

(*c*) The displacement of hydrogen by the interaction of (1) zinc and hydrochloric acid, (2) magnesium and acetic acid, (3) lead and sulfuric acid, (4) calcium and phosphoric acid, (5) sodium and water, (6) iron and steam.

(*d*) The displacement reaction between zinc metal and copper sulfate solution.

(*e*) The production of elemental metals by the reactions between (1) copper oxide and hydrogen, (2) ferric oxide and hydrogen, (3) ferric oxide and carbon monoxide, (4) lead monoxide and carbon monoxide.

9. When sodium iodide is added to an excess of concentrated sulfuric acid, elemental iodine and hydrogen sulfide gas are produced. Write the equation for this reaction.

10. Gaseous sulfur dioxide is liberated by the interaction of ferrous sulfate and concentrated sulfuric acid. Write the corresponding equation.

11. On the assumption that all of the combined sulfur involved is changed to elemental sulfur, write the equation for the reaction between H_2S and concentrated H_2SO_4.

12. The reduction of iodine by sodium thiosulfate ($Na_2S_2O_3$) results in the formation of sodium tetrathionate ($Na_2S_4O_6$). Write the equation for this reaction.

13. If copper sulfide is treated with warm dilute nitric acid, the CuS is dissolved and S^0 and gaseous NO are produced. Write equations to represent these changes.

14. Write an equation showing the formation of sodium thiosulfate by the interaction of sodium sulfite solution and elemental sulfur.

15. Write equations for the following indicated oxidation-reduction reactions:

(*a*) $NH_3 + O_2 \rightarrow NO + H_2O$
(*b*) $MnO_2 + Al \rightarrow Al_2O_3 + Mn$
(*c*) $H_2O_2 \rightarrow H_2O + O_2$
(*d*) $FeCl_3 + H_2S \rightarrow FeCl_2 + S +$
(*e*) $Cu + Hg_2(NO_3)_2 \rightarrow Cu(NO_3)_2 + Hg$
(*f*) $C + HNO_3 \rightarrow CO_2 + NO_2 + H_2O$
(*g*) $H_2O_2 + H_2SO_4 \rightarrow H_2S_2O_8 + H_2O$
(*h*) $NaBr + NaBrO + H_2SO_4 \rightarrow Br_2 +$
(*i*) $Ca(ClO)_2 \rightarrow Ca(ClO_3)_2 + CaCl_2$
(*j*) $I_2 + H_2SO_3 + H_2O \rightarrow HI + H_2SO_4$
(*k*) $SnCl_2 + K_2Cr_2O_7 + HCl \rightarrow SnCl_4 + CrCl_3 +$
(*l*) $Al + NaNO_3 + NaOH + H_2O \rightarrow NaAlO_2 + NH_3$

16. What is necessary for the occurrence of a metathetical reaction?

17. If a metathetical reaction occurs, what determines the extent to which it goes toward completion?

18. For the following pairs of similar metathetical reactions, indicate in each case which proceeds most nearly to completion and cite reasons for the answers given:

(*a*) Sodium sulfate + silver nitrate
(*b*) Sodium sulfate + lead nitrate

(*a*) Potassium sulfide + sulfuric acid
(*b*) Potassium cyanide + sulfuric acid

(*a*) Hydrochloric acid + barium hydroxide
(*b*) Sulfuric acid + barium hydroxide

19. Write equations for the following indicated metathetical reactions. In each case, mark all strong electrolytes, all insoluble substances, predict whether the reaction will occur, and state the basis for each prediction:

(*a*) Lead nitrate + hydrochloric acid
(*b*) Strontium chloride + ammonium acetate
(*c*) Copper sulfate + sodium phosphate
(*d*) Mercuric nitrate + sodium cyanide
(*e*) Zinc chloride + potassium sulfate
(*f*) Phosphoric acid + aluminum hydroxide
(*g*) Nickel nitrate + sodium iodide
(*h*) Ferric chloride + potassium thiocyanate
(*i*) Ammonium sulfate + sodium hydroxide
(*j*) Lead chloride + sodium acetate

SUGGESTED READING

Journal of Chemical Education

Hall, Oxidation-reduction Reactions, **6**, 479 (1929).
Brinkley, Typical Oxidation-reduction Reactions in General Chemistry, **6**, 1894 (1929).
Jette and LaMer, The Balancing of Oxidation-reduction Equations, **4**, 1021, 1159 (1927).
Lochte, Electromotive Force Table and Oxidation-reduction Reactions, **10**, 373 (1933).
Bennett, Balancing Equations by the Valence-change Method, **12**, 189 (1935).
Morris, The Balancing of Oxidation-reduction Equations, **15**, 538 (1938).
Lawrence, Short Cuts in Balancing Oxidation-reduction Equations, **17**, 388 (1940).
Glasstone, Oxidation Numbers and Valence, **25**, 278 (1948).
Heimerzheim, Solubility Generalizations, **18**, 377 (1941).

CHAPTER 18

COLLOIDS

Emphasis has already been placed upon the properties of matter in each of the three physical states and in solutions. There remain to be considered the characteristics of solids, liquids, and gases in a state of existence known as the *colloidal condition* or *colloidal state*. The various combinations of solids and liquids, liquids and liquids, liquids and gases, etc., in the colloidal condition are called *colloids* and exhibit certain similarities to true solutions. On the other hand, colloids and solutions differ in many important respects.

18.1. Nature of Colloids

The term *colloid* is derived from the Greek word *kolla* which means glue, a term rather generally suggestive of the character of many (but not all) colloids. The term *colloid* is applied to many intimate mixtures of two or more substances which are usually very finely divided and mutually insoluble. Perhaps the best means of gaining some idea as to the over-all nature of those materials commonly classified as colloids is to cite some familiar examples. Such common materials as milk, ink, egg white, gelatin, glue, soap, "milk of magnesia," and many foodstuffs, medicinals, etc., are colloidal in character. Processes such as the treatment of municipal water supplies, sewage disposal, preparation of soils for road building, drilling of oil wells, manufacture of clay products, and smoke abatement, either involve the use of colloidal materials or are dependent upon a knowledge of the properties of matter as it exists in the colloidal condition.

Distinction between Colloids and Solutions. From the recognition that confusion is likely to result from certain similarities between colloids and solutions, it seems necessary to draw a clear distinction between the two before proceeding with any detailed study of colloids.

It may be recalled that a true solution consists of a solvent in which is dissolved a solute in the form of units which usually are not larger than single molecules. Frequently when two true solutions are mixed, these molecules react to form an insoluble solid, the molecules of which collect to form particles large enough to settle to the bottom of the

container under the influence of gravity. But occasionally one finds that the insoluble solid particles that form are so small that they either settle out extremely slowly or remain suspended in the liquid indefinitely. Such a system, consisting of very small particles of a solid suspended throughout the body of a liquid, is classed as a colloid. The suspended particles of solid are larger than single molecules and consist of clusters of molecules or atoms which, for reasons that are indicated later, remain suspended in the liquid.

A similar result may also be realized by starting with a large particle of a solid and subdividing this solid until the particles become so small that they remain in suspension. For example, a cube of gold having edges 1 cm. in length and therefore an exposed surface area of 6 sq. cm. would, of course, not remain suspended in water. If, however, this cube is divided into cubes having edges only 0.01 cm. in length, the total number of such cubes would be $100 \times 100 \times 100$ or 10^6 cubes. Since each of these cubes has a surface area of

$$6 \times (0.01)^2 = 6 \times 10^{-4} \text{ sq. cm.}$$

the total surface area exposed by all these cubes would be

$$10^6 \times 6 \times 10^{-4} = 600 \text{ sq. cm.}$$

an area one hundred times as great as that of the original cube. Upon being mixed with water, cubes of this size would also settle to the bottom of the container, but if the process of subdivision were continued until the cubes were so small that the total exposed surface area was about one million times as great as that of the original cube, the particles would then be so small that they would remain suspended in water in the colloidal condition. This process of subdivision would, of course, involve a tremendous increase in exposed surface (as compared with that of the original cube), and, as is shown later, this fact has an important bearing upon the properties of matter in the colloidal state.

Dimensions of Colloidal Particles. With reference to the preceding example, it becomes of interest to calculate the number of cubes into which the original cube would have to be subdivided in order to produce colloidal gold. Since the *average* diameter of colloidal particles is *approximately* 10^{-6} cm., the required number of cubes would be $10^6 \times 10^6 \times 10^6 = 10^{18}$ cubes, each having edges 10^{-6} cm. in length and a surface area of $6 \times (10^{-6})^2$ or 6×10^{-12} sq. cm. Accordingly, the total area exposed by the 10^{18} cubes would be

$$10^{18} \times 6 \times 10^{-12} = 6 \times 10^6 \text{ sq. cm.}$$

or, as indicated above, an area one million times as great as that of the original cube and about one-seventh the area of a football field.

Although the dimensions of colloidal particles could be expressed in centimeters or millimeters, there has been adopted another unit, the *millimicron*, more suited to the expression of small lengths. The millimicron is represented by the symbol mμ, and is equal to one one-millionth of a millimeter (*i.e.*, 10^{-6} mm.).

The largest known molecules have diameters of approximately 1 mμ; hence, any particle having a diameter of 1 mμ, or less, would exist in water (or other solvent) in true solution. Particles having diameters within the range of 1 to 100 mμ are, in general, considered to be of colloidal size. Particles of diameter greater than 100 mμ would, in general, be too large to remain suspended in the colloidal cond tion. Incidentally, particles having diameters of about 150 mμ represent the smallest objects that can be seen by means of an ordinary microscope. The foregoing relationships may be clarified by the accompanying chart.

DIMENSIONS OF PARTICLES OF MATTER

		1 mμ	100 mμ
Approximate diameter	←	←	→
Nature of particles	Molecules, Atoms, Ions	Colloidal	Larger than colloidal
Mode of existence in presence of a solvent	In true solution	In colloidal suspension	Settle under influence of gravity

Types of Colloids. From the preceding discussion, it becomes rather apparent that a colloidal system must consist of a mixture of at least two materials. By analogy with the various possible varieties of true solutions, it would appear that nine combinations might be possible. However, since mixtures of gases are always homogeneous and mutually soluble, colloidal systems consisting of gases in gases are not possible. Of the eight remaining theoretically possible colloidal systems several are relatively uncommon.

In the language of the chemistry of colloids, the particles (solid, liquid, or gas) and the medium (solid, liquid, or gas) in which the particles exist in the colloidal condition are known as *phases*. The colloidal particles are referred to as being the *dispersed phase*, and the medium in which they are dispersed is called the *dispersion medium*. In terms of these two components, the most common types of colloidal systems are listed in Table 23 on page 260.

Before leaving the subject of the general nature of colloidal materials, it should be understood clearly that the existence of matter in the

colloidal condition is largely independent of the *kind* of matter involved. For example, many chemical substances that exist in water in the form of true solutions under one set of experimental conditions may, under another set of conditions or in another liquid, exist in the colloidal condition. The properties of matter in the colloidal state are largely dependent upon the *state of subdivision* of the colloidally dispersed materials.

TABLE 23

Common Types of Colloidal Systems

Dispersed phase	Dispersion medium	Example
Solid	Liquid	Colloidal gold in water
Solid	Gas	Smoke (particles of carbon in air)
Liquid	Gas	Fog (water droplets in air)
Liquid	Liquid	Emulsions (such as oil in water)
Gas	Liquid	Foams

18.2. Preparation of Colloids

The available methods whereby colloids may be produced have already been suggested (Sec. 18.1) and may be classified broadly as *condensation* methods and *dispersion* methods.

Condensation. As is suggested by the term itself, condensation methods involve starting with single molecules and bringing them together in sufficient number to build up particles having diameters within the range of 1 to 100 mμ. A familiar example of the application of this method is found in the formation of a fog or mist by the rapid expansion of moist air. Upon being cooled by expansion (Sec. 7.2), the water molecules collect to form small droplets of colloidal size. By striking an electric arc between metal electrodes held under water or other suitable liquid, the metal is vaporized by the arc and the vapors condense to form particles many of which are within the range of the dimensions of colloidal particles. Lead, silver, copper, platinum, gold, and other metals have been dispersed successfully by this procedure. Colloidal gold may be so produced in such a finely subdivided condition that the colloidal particles settle (under the influence of gravitational attraction) only through a distance of a little more than 1 cm. over a period of 10 years.

This process of building up colloidal particles from single molecules, atoms, or ions, is perhaps most commonly illustrated by reactions between electrolytes in true solutions. Yellow colloidal arsenious sul-

fide may be formed by the metathetical reaction between arsenious acid and hydrogen sulfide.

$$2H^+AsO_3^- + 3H_2S \rightarrow 4H_2O + \underline{As_2S_{3(colloidal)}}$$

Similarly, reddish-brown colloidal ferric hydroxide may be produced by the metathetical reaction between ferric chloride and water,

$$Fe^{+++}Cl_3^- + 3H_2O \rightarrow 3H^+Cl^- + \underline{Fe(OH)_{3(colloidal)}}$$

Oxidation-reduction reactions also may be employed. Thus, brown or black colloidal nickel may be formed by heating a solution of nickel carbonyl in benzene.

$$\begin{array}{ll} (a) & 4(CO)^- - 4e^- \rightarrow 4CO \\ (b) & Ni^{++} + 4e^- \rightarrow Ni \\ \hline (c) & Ni(CO)_4 \rightarrow 4CO + \underline{Ni_{(colloidal)}} \end{array}$$

Colloidal sulfur may be prepared by the interaction of hydrogen sulfide and sulfurous acid.

$$\begin{array}{ll} (a) & 2S^{--} - 4e^- \rightarrow 2S \\ (b) & S^{++} + 4e^- \rightarrow S \\ \hline (c) & 2S^{--} + S^{++} \rightarrow 3S \\ (d) & 2H_2S + H_2SO_3 \rightarrow 3H_2O + \underline{3S_{(colloidal)}} \end{array}$$

Many other metathetical and oxidation-reduction reactions may be employed similarly in condensation methods for the preparation of elements or compounds in the colloidal condition.

Dispersion. The process of producing colloids by starting with large particles and breaking them down into particles of colloidal size is known as *dispersion* or *peptization*. This type of method is illustrated by the following examples:

1. In recent years mechanical grinding machines (*colloid mills*) have been invented for this purpose and are remarkably effective in producing colloidal particles having diameters as small as 50 mμ.

2. Colloids consisting of liquids dispersed in liquids may sometimes be prepared merely by shaking the two liquids together either manually or by mechanical agitation. Mixtures of butterfat and milk may be rendered colloidally homogeneous ("homogenized") by subjecting the mixture to high pressures and forcing the mixture through a very fine orifice. The fat globules are thereby dispersed uniformly throughout the body of the liquid milk.

3. In one sense, the production of colloidal metals by the use of an electric arc may be classified as a dispersion method since dispersion of the metal in the form of vapor must necessarily precede condensation of these vapors.

4. Some substances are peptized merely by contact with a suitable dispersion medium. For example, materials such as glue and gelatin are peptized upon contact with water and thereupon assume a colloidal condition rather than dissolving to form true solutions. Similarly, when one attempts to wash (with water) freshly precipitated zinc sulfide on an ordinary filter paper, the sulfide is frequently peptized by the water and the colloidal particles pass through the small pores in the filter paper.

18.3. Purification of Colloids

The stability of a colloid is often influenced adversely by the presence of molecules or ions dissolved in the dispersion medium. Consequently, in order to stabilize a colloid, it may become necessary to subject it to a purification process known as *dialysis*. This procedure is carried out by enclosing the colloidal system in a membrane such as parchment paper or collodion, and immersing the bag and its contents in pure solvent, *e.g.*, water, as shown in Fig. 78. The dissolved impurities diffuse through the membrane and may be progressively removed by providing for continuous introduction of fresh water. Owing to the fact that either the membrane is selectively permeable only by solute particles or that the solute particles diffuse much more rapidly than the larger colloidal particles, an extended dialysis is frequently very effective as a means of purification. This method is used largely in the purification of colloids consisting of solids dispersed in liquids.

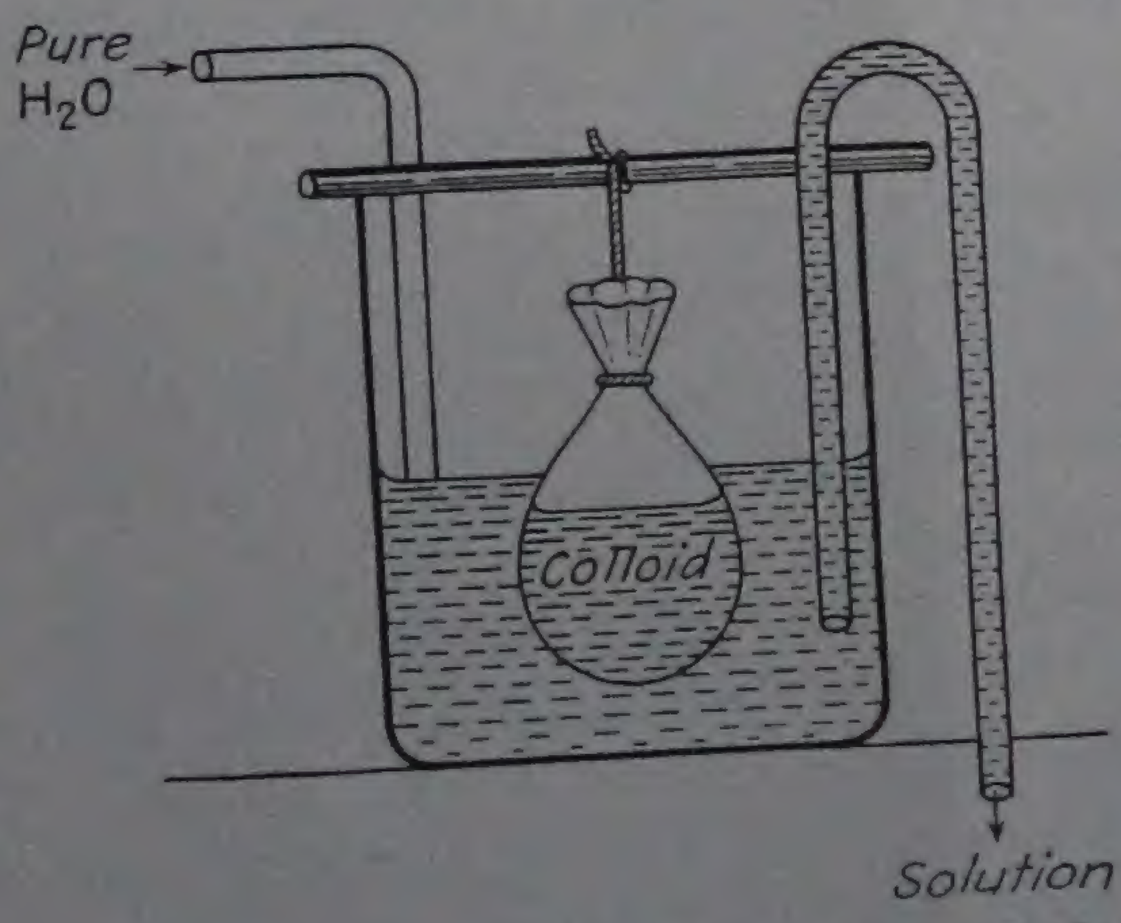

FIG. 78. A simple illustration of the process of dialysis.

18.4. Properties of Matter in the Colloidal Condition

Two important characteristics of colloids have already been considered, *i.e.*, the dimensions of colloidal particles and the tremendous

surface area exposed by a given weight of matter in the colloidal condition. Several other properties are, in some measure, shared by colloids in general, and these properties are useful in identifying and characterizing colloids.

Tyndall Effect. When a strong beam of light is passed through a solution, the path of the beam is not visible to the unaided eye. If, however, this beam of light is passed through a colloid, the small colloidal particles act as reflectors, and the path of the beam is visible as a turbid cone (Fig. 79). Named for the scientist who first observed and described it, this phenomenon is known as the *Tyndall effect*, and the visible path of the light is known as a *Tyndall cone*. The same sort of effect is commonly observed when a beam from a searchlight passes through a fog, mist, or smoke.

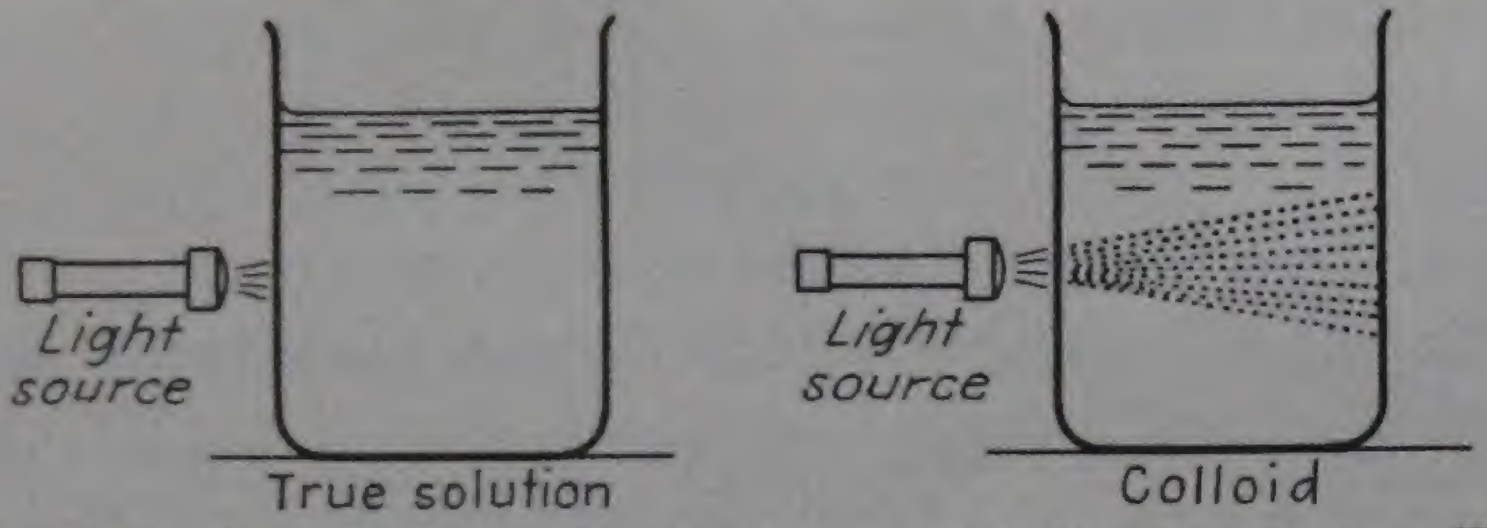

FIG. 79. Tyndall effect. The path of a beam of light appears as a Tyndall cone in the case of a colloid but not in the case of a true solution.

Brownian Movement. If a Tyndall cone is viewed through a microscope placed at right angles to the beam of light, the motion of the light reflected from the colloidal particles gives evidence that the particles are in motion (Fig. 80) owing to their inherent kinetic energy. Such a device is known as an *ultramicroscope* and enables the observer to view the unordered motion of colloidal particles which are not much larger than some molecules. The unorderly nature of the movement of colloidal particles results from their collisions with each other, with molecules of the dispersion medium, or with the walls of the container. This was first observed in 1827 by the Scotch botanist Robert Brown and has since been known as *Brownian movement*. The French chemist Jean Perrin found it possible to measure directly the size, mass, and velocity of motion of certain colloidal particles. From these data, the kinetic energies of the particles were calculated. Perrin found that, *at any given temperature, the average kinetic energy is the same*

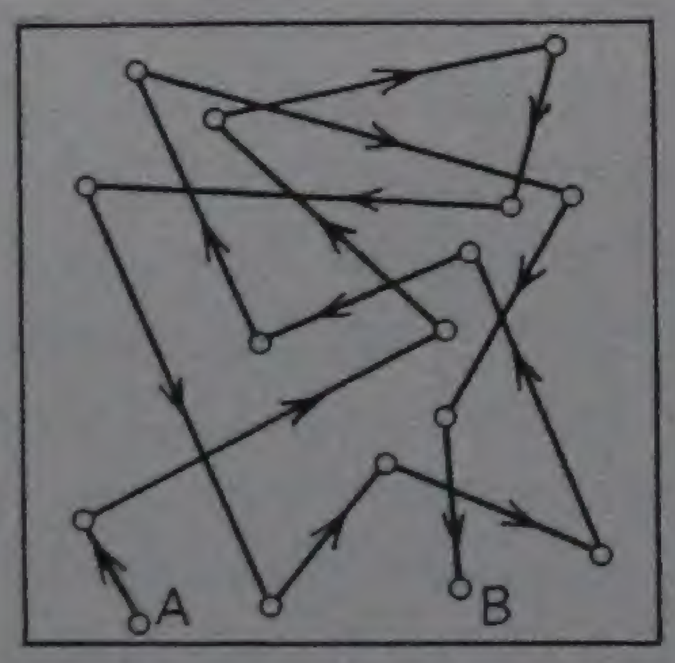

FIG. 80. Illustration of Brownian movement.

for particles of widely different mass and of the same order of magnitude as the average kinetic energy of gas molecules at the same temperature. It is of interest to consider these striking results in the light of the kinetic-molecular theory and to recognize that the inherent kinetic energy of the individual particles is an important factor bearing upon the stability of colloidal systems.

Electrical Properties. When a colloid is placed in the space between two electrodes arranged in a cell, such as that shown in Fig. 81, and a relatively high voltage is employed, the colloidal particles migrate slowly toward either the positive or the negative electrode. Colloidal metals and metal sulfides usually migrate toward the positive electrode; hence, it is concluded that these particles must bear a *negative* charge. Correspondingly, most colloidal hydroxides of the metals move toward the negative electrode, a fact that indicates that these colloidal particles bear a *positive* charge. The magnitude of the electrical charges borne by colloidal particles is far greater than the charges of individual ions, and the relatively slow migration of these particles is attributed to their relatively great size. Since colloidal particles usually consist of clusters of *electrically neutral* atoms or molecules, there arises immediately a question as to the origin of the charges possessed by colloids. The answer to this question requires some additional information concerning the subject of adsorption.

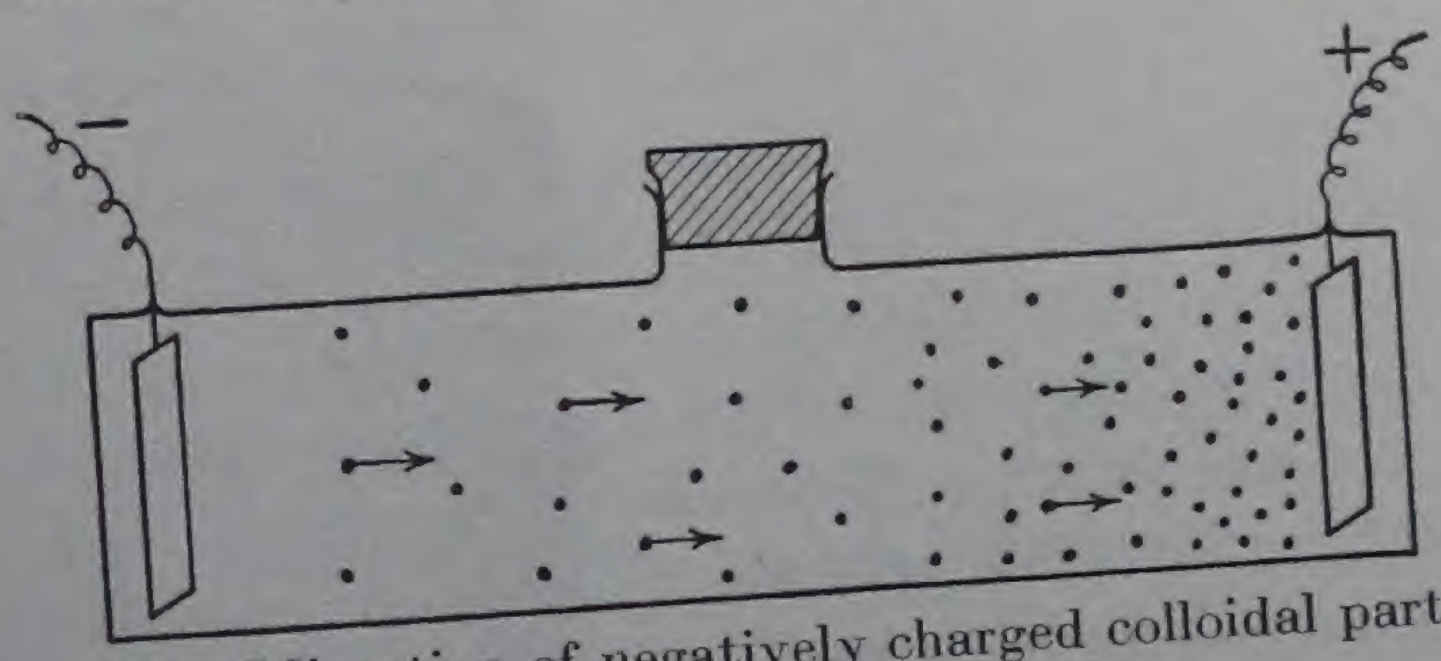

FIG. 81. Migration of negatively charged colloidal particles.

Adsorption. Although the molecules in the interior of a colloidal particle are attracted equally in all directions by other molecules, those on the surface of a colloidal particle are in a condition similar to that experienced by molecules in the surface of a liquid (Sec. 7.3), *i.e.*, they are subject to unequal forces of attraction. Since colloidal particles possess great surface area, there are many such molecules in the surface of a single particle. Colloids and other finely divided forms of matter therefore have the property of attracting and holding other molecules, atoms, or ions on their surfaces; this is the phenomenon of *adsorption*.

Adsorption plays an important role in many processes including the adsorption of poisonous gases on the charcoal contained in gas masks, the flotation of ores (Sec. 22.2), the bleaching of cottonseed oil by means of fuller's earth, etc.

Suspensoids. The electrical charge borne by colloidal particles is due to the adsorption of ions from the surrounding medium. As is true of adsorption in general, the adsorption of ions by colloidal particles is highly selective. That is, a given colloidal particle may adsorb positive ions and not negative ions, while with other kinds of colloids, the reverse is true. Since colloidal particles of any particular kind all adsorb ions of the same charge, these particles tend to prevent coagulation and hence contribute to the stability of colloidal systems. *Colloids in which the dispersed phase consists of particles that selectively adsorb ions from the dispersion medium are known as suspensoids.* The viscosity of a suspensoid is usually not greatly different from the viscosity of the dispersion medium.

Emulsoids. In contrast to suspensoids, there are colloids which are less selective with regard to the adsorption of ions and which exhibit a marked tendency to adsorb molecules of the dispersion medium as well as ions. Such colloids are known as *emulsoids.* As the particles continue to adsorb molecules of the dispersion medium, they appear to swell, and this swelling process may continue until the entire system assumes a semirigid condition such as exists in glues, jellies, etc. This swelling process is commonly observed when dried fruits are placed in contact with water. In semiarid regions, certain forms of plant life retain moisture over long periods of time because they contain colloids that are capable of adsorbing water to an unusual extent. In any event, the extent of adsorption of the dispersion medium depends upon the specific character of the emulsoid, the temperature, and the acidity of the environment. It is rather apparent that the viscosity of an emulsoid is usually much greater than that of the dispersion medium.

18.5. Jellies and Gels

The adsorption of molecules of the dispersion medium by the colloidal particles in an emulsoid may continue until most of the dispersion medium has been adsorbed. As this process continues, the colloid becomes increasingly viscous and finally sets to a semirigid mass which is commonly described by the term *jelly.* Familiar examples include fruit jellies, in which a substance known as *pectin* yields the emulsoid particles that adsorb the colored and sweetened water solution serving

as the dispersion medium. Jelly formation is involved also in the preparation of gelatin deserts.

If the dispersion medium is removed from a jelly, the resulting amorphous solid material frequently possesses a very porous structure and is called a *gel*. If water or alcohol, for example, is the dispersion medium, a jelly may sometimes be converted to a gel simply by cautious application of heat. Silica gel (SiO_2) and alumina gel (Al_2O_3) may be produced in this manner. Gels commonly have a structure somewhat like that of a sponge or honeycomb. Accordingly, gels present relatively great exposed surfaces and are rather commonly used as carriers for catalysts, as deodorants, and as adsorbents for other purposes.

18.6. Coagulation of Colloids

Colloids are produced in the laboratory and commercially because such substances possess useful properties. On the other hand, it is frequently true that in an effort to form precipitates, the objective is not realized because the material desired in the form of a precipitate actually appears in the colloidal condition. Consequently, it may be just as important to know how to destroy (or coagulate) colloids as it is to know how to produce them. Disturbance of those factors which are responsible for the stability of a colloid usually results in coagulation (or precipitation). In general, suspensoids are more easily coagulated than emulsoids.

Coagulation of Suspensoids. Since the electrical charge borne by suspensoid particles is the chief factor responsible for the stability of suspensoid colloids, neutralization of this charge usually results in precipitation. Addition of an electrolyte is commonly effective in causing coagulation at ordinary temperatures and more effective at elevated temperatures. Upon neutralization of the charges on the suspensoid particles, there is no longer an electrical repulsion of one particle by another, and the particles collect upon collision until the Brownian movement is no longer capable of keeping these enlarged particles in suspension. Elevation of the temperature serves to increase the kinetic energy of the particles, which results in increased frequency of collision and consequently accelerates the coagulation process. The valence of the ion of the precipitating electrolyte has a marked bearing upon its efficiency. A divalent ion is many times more effective than a univalent ion, and a trivalent ion is often hundreds of times more effective than a univalent ion. Thus, in the coagulation of the negatively charged particles of arsenious sulfide,

aluminum ion (Al^{+++}) would be more effective than calcium ion (Ca^{++}), which in turn would be more effective than sodium ion (Na^{+}).

If suspensoids of opposite charge are brought together, coagulation usually occurs as the result of *mutual* neutralization of charges. Thus, the mixing of a positively charged ferric hydroxide suspensoid and a negatively charged arsenious sulfide suspensoid results in precipitation of both.

Coagulation of Emulsoids. The stability of an emulsoid is due to (*a*) the electric charge borne by the emulsoid particles and (*b*) the layers of adsorbed dispersion medium on the surface of the emulsoid particles. As is true of any colloid, the coagulation of emulsoids may be accomplished by elimination of the factors responsible for their stability. For example, if water is the dispersion medium, the emulsoid particles may often be stripped of adsorbed molecules by an elevation of temperature (boiling) or by the addition of a dehydration agent such as alcohol. Once this has been accomplished, neutralization of the electrical charge usually results in complete coagulation. Sometimes, heating alone accomplishes coagulation; in other cases the addition of a dehydrating agent (without heating) is effective.

18.7. Emulsions

When two mutually insoluble liquids, such as kerosene and water, are thoroughly shaken together, the resulting mixture consists of tiny droplets of the two liquids dispersed throughout each other. Owing to the surface-tension forces (Sec. 7.3) that cause liquids to tend to present the least possible exposed surface, the small drops of kerosene and water will, upon standing, coalesce into larger and larger drops until finally the water and kerosene separate into two distinct layers. Some such dispersions, however, are stable, while in other cases the addition of a third substance is necessary for stabilization. Such a colloidal dispersion of one liquid in another is called an *emulsion*. The stabilizing action of the added substance usually depends upon its ability to lower the surface tension of the liquids concerned. Substances employed in the stabilization of emulsions are known as *emulsifying agents*. Occasionally stable emulsions are produced when two liquids are mixed because one of the liquids contains an impurity that acts as an emulsifying agent.

Numerous examples of useful emulsions might be cited. Milk, mayonnaise, certain lubricants, etc., are familiar examples. Soap is rather commonly used as the emulsifying agent in the formation of oil-water emulsions. If a sodium soap is employed, the oil is dis-

persed throughout the body of the water, while use of a calcium soap results in an emulsion in which the water is the dispersed phase and the oil is the dispersion medium. The cleansing action of a soap is an interesting example of the formation of emulsions. The dirt on the hands, for instance, is usually surrounded by a thin film of grease or oil. Water does not emulsify this oil or grease, but soap lowers the surface tension between the water and oil and thus results in the formation of a stable emulsion which encloses the particles of dirt, and the whole may then be rinsed away with water.

18.8. Applications of Colloids

At various points in the preceding discussion, numerous examples of the use of materials in the colloidal condition have been cited. Some additional applications of considerable importance remain to be considered.

Smoke Abatement. Smoke consists of fine particles of carbon dispersed colloidally in a gaseous dispersion medium, the air. The problem of eliminating smoke nuisances resulting from smoke production in chemical and other manufacturing plants, particularly where bituminous coal is used as a fuel, was solved by the American chemical engineer F. G. Cottrell in 1911. The Cottrell process involves passing the smoke between two electrically charged plates. The charged colloidal particles are attracted to the plate bearing the opposite charge, and upon neutralization of the charge borne by the particles of carbon, they coagulate to form grains too large to exist in the colloidal condition. This results not only in the substantially complete elimination of the smoke nuisance but also in the recovery of considerable quantities of carbon, which may be used as a fuel or for other purposes.

Formation of Deltas. When the muddy waters of a fresh-water stream flow into a body of "salt water," the colloidal materials in the muddy water are precipitated by the high concentration of dissolved electrolytes in the sea water. Thus, the vast reaches of the Mississippi delta region have been built up, at least in part, by the coagulating action of electrolytes present in the waters of the Gulf of Mexico. This factor has, therefore, an important bearing on the navigability of waters near the mouths of rivers.

Vital Processes. The subject of colloid chemistry is particularly important to students of botany, biology, and medicine, since all vital processes of plants and animals are intimately concerned with colloidal materials. The germination of seeds, the growth of plants, and the very structures of the plants themselves involve complex colloidal materials to a predominant extent. The protoplasm that is the basis of all

animal life is essentially colloidal in character. Furthermore, most foodstuffs essential to the maintenance of animal life are colloids of one kind or another.

Protective Colloids. In the commercial production of colloidal products, stabilization is often accomplished by addition of so-called *protective colloids*, which are usually emulsoids. Thus, in forming mayonnaise salad dressing an emulsion of a salad oil (olive oil, cotton-seed oil, etc.) in vinegar (a dilute water solution of acetic acid) is stabilized by the addition of egg yolk. The smooth texture of good-quality ice cream may be produced by adding gelatin, which serves as a protective colloid, while gum arabic serves the same purpose in marshmallows. In the manufacture of india ink, colloidal carbon is stabilized by the use of protective colloids consisting of various gums. Certain useful lubricants consist of colloidal graphite stabilized by tannin, a protective colloid which also finds extensive use in the ceramic industries.

GENERAL EXERCISES

1. What is the essential difference between (*a*) suspensoids and emulsoids, (*b*) emulsoids and emulsions, (*c*) colloids and true solutions, (*d*) jellies and gels?
2. Define the following terms: (*a*) dialysis, (*b*) protective colloid, (*c*) emulsifying agent, (*d*) ultramicroscope, (*e*) Tyndall effect, (*f*) Brownian movement, (*g*) millimicron, (*h*) dispersed phase, (*i*) dispersion medium, (*j*) adsorption.
3. Make a list of at least 10 natural or artificial materials that are colloidal in character.
4. With regard to colloids, list methods that are useful practically in (*a*) preparation, (*b*) purification, (*c*) stabilization, and (*d*) coagulation, and indicate briefly the characteristic features of these methods.
5. Draw an enlarged diagram of an emulsoid particle in a manner that will serve to explain why the addition of an electrolyte might fail to coagulate such a colloid.
6. To what properties do the various types of colloids owe their stability?
7. In what respects are colloidal particles and gas molecules similar?
8. In the study of colloids, why is the property of viscosity of importance?
9. What is meant by the mutual precipitation of colloids?
10. If a negative colloid is to be precipitated by the addition of an electrolyte, which, of course, furnishes both positive and negative ions, why is it that the addition of negative ions does not further stabilize the colloid and thus counteract the precipitating action of the positive ions?
11. If one wished to coagulate a positive colloid by the addition of an electrolyte, what electrolytes would be most effective?

SUGGESTED READING

Journal of Chemical Education

McBain, Structure in Amorphous and Colloidal Matter, 6, 2115 (1929).
McBain, Some Recent Advances in Colloids, 17, 109 (1940).

Elder, Red Gold Sols, **17,** 512 (1940).
Hauser, Colloids in Your Daily Life, **18,** 590 (1941).
Morris, How Many Colloids Have You Used Today? **3,** 438 (1926).
Bray, Aerosols—Clouds, Dust, Fog, and Smoke, **6,** 1486 (1929).
Zimmerman, The Application of Colloidal Chemistry to Foods, **3,** 1282 (1926).
Gortner, Colloids in Biochemistry, **11,** 279 (1934).
Travis, Colloids in Industry, **3,** 324 (1926).
Szymanowitz, An Application of Colloid Chemistry to Lubrication, **3,** 909 (1926).
Hauser, The Nomenclature of Colloid Chemistry, **25,** 367 (1948).
Damerell and Brock, Colloidal Gardens from Sodium Metasilicate, **26,** 148 (1949).

CHAPTER 19

ELECTROLYSIS

The use of electrical conductance as an aid in determining whether certain solutes should be classified as electrolytes or nonelectrolytes (Sec. 14.2) together with references to the use of electricity in the decomposition of certain compounds (Sec. 9.6) suggests that electrical energy often may be used to advantage in chemistry. In fact, it may be stated that both in the laboratory and in the chemical industries, electricity is one of the most important tools that the chemist has at his command. Following a study of the nature of the chemical changes that may be brought about through the agency of electrical energy, numerous important commercial applications are considered in some detail.

19.1. Electrolytic Cells

The process of **electrolysis may be defined as the transformation of chemical substances as the result of passage of the direct electric current.** In order to bring about such transformations, the use of certain more or less highly specialized apparatus is necessary or at least convenient. A simple form of electrolytic cell is illustrated by Fig. 82. The cell as a whole consists of a vessel containing a solution of an electrolyte in which are immersed two electrodes (or poles). The electrodes are connected to storage batteries or to a generator which serve as sources of the electrical energy needed to bring about the desired electrolytic transformation. The electrode through which the flow of electrons enters the cell is known as the *cathode* and is designated as the *negative* (−) electrode. By convention, the other electrode, which is called the *anode*, may be thought of as that through which electrons are withdrawn from the solution, and this electrode is designated as *positive* (+). Throughout the following sections, the terms *cathode* and *anode* are used to designate the negative and positive electrodes, respectively.

It must be recognized that Fig. 82 is only a highly simplified representation of an electrolytic cell. Actual commercial practice usually employs a connected series of such cells constructed in such manner as

to meet the needs of each specific operation. Frequently the vessel containing the electrolyte is made of metal and serves as one of the electrodes. Other modifications are shown in connection with commercial applications of electrolysis.

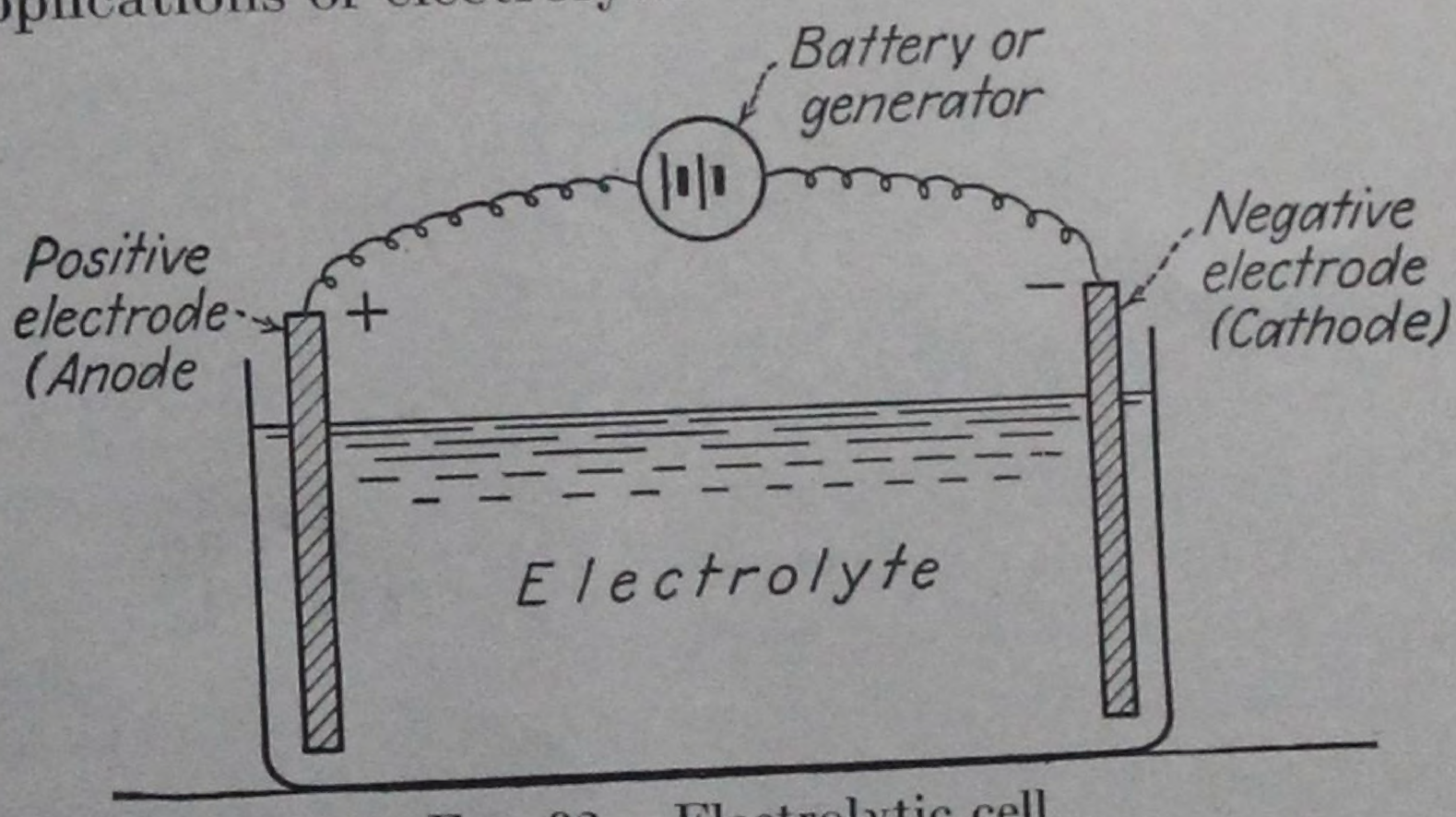

FIG. 82. Electrolytic cell.

19.2. Electrolysis of Zinc Chloride Solution

The occurrence of a simple electrolysis may be demonstrated conveniently by passing a direct current through an aqueous solution of zinc chloride. A rectangular glass vessel (Fig. 83) is filled partly with zinc chloride solution. A polished strip of brass serves as the cathode while a carbon rod constitutes the anode. In this particular case, the

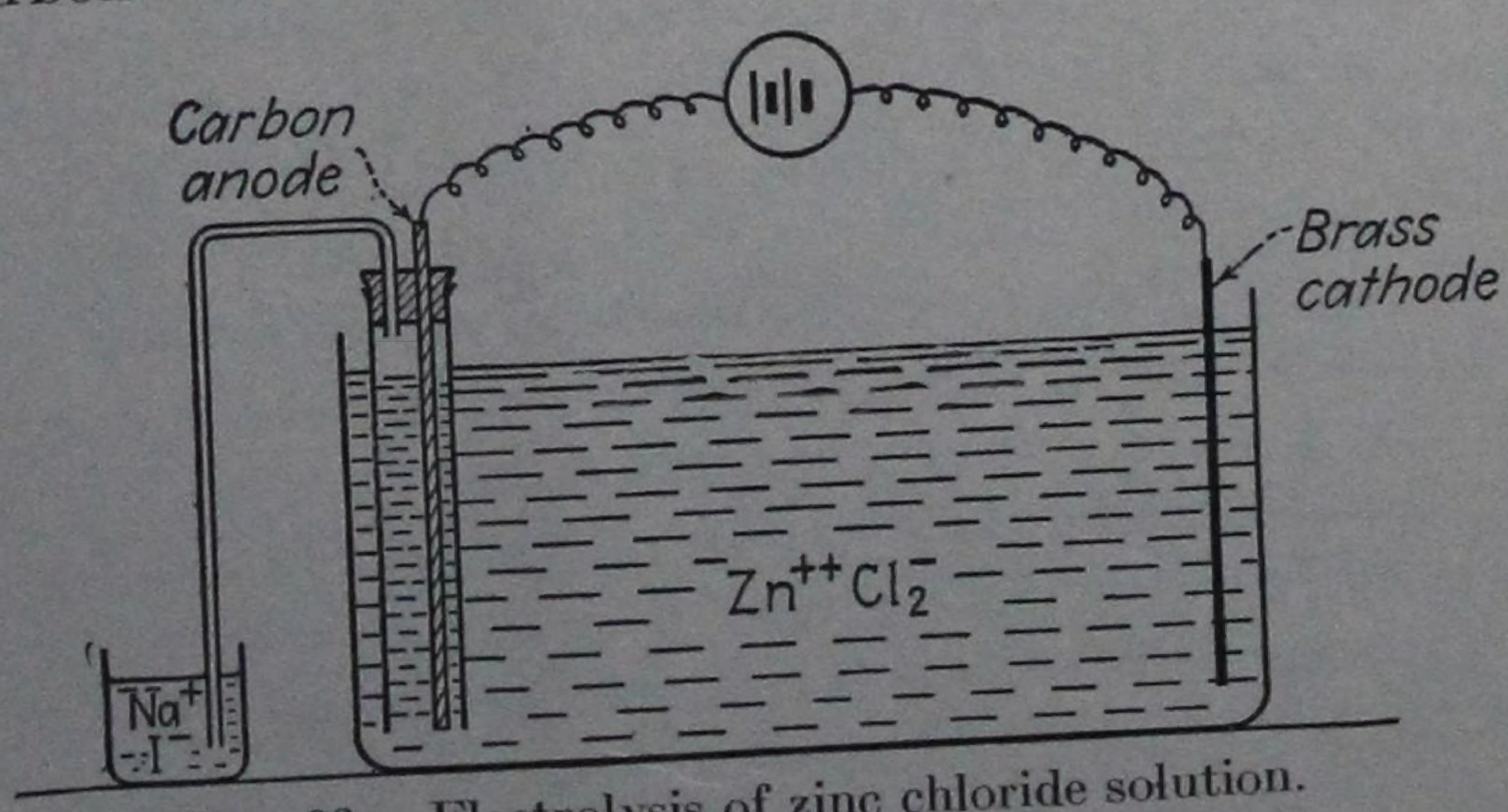

FIG. 83. Electrolysis of zinc chloride solution.

use of a carbon rod rather than a metal is advisable since most metals would react chemically with one of the products of the electrolysis, thus complicating the situation with secondary reactions not concerned with the primary process of electrolysis. Further, it is convenient to surround the anode with a glass housing in which the gaseous electrolysis product may be collected and from which it may be continuously withdrawn through a suitable exit tube.

Immediately upon connecting the cell to a source of direct current, a deposit of gray metallic zinc appears on the surface of the cathode and bubbles of chlorine gas appear at the surface of the anode. A simple chemical test for chlorine may be made by leading this gas into aqueous sodium iodide solution, whereupon the solution assumes a yellow color caused by displacement of iodine by chlorine (Sec. 16.4). Accordingly, it is concluded that the products of the electrolysis of zinc chloride solution are elemental zinc and elemental chlorine, and the next problem is that of explaining by what mechanism these products may be produced.

The solution in the cell contains zinc ions (Zn^{2+}) and chloride ions (Cl^-). The chloride ions are attracted to the anode (+ electrode) where they give up electrons and form molecules of elemental chlorine.

$$\text{At anode: } 2Cl^- - 2e^- \rightarrow \overline{Cl}_2$$

The battery acts as a "pump" and forces these electrons through the outside circuit and into the cathode, at the surface of which these electrons are acquired by the zinc ions in the solution surrounding the cathode, *i.e.*,

$$\text{At cathode: } Zn^{2+} + 2e^- \rightarrow \underline{Zn}$$

Obviously, these reactions involve loss and gain of electrons and therefore are to be recognized as oxidation-reduction reactions (Sec. 17.1). The sum of the changes that occur in the regions of the anode and cathode serves to represent the over-all chemical change that occurs in the cell as a whole, *i.e.*,

$$\begin{aligned} \text{Anode: } & 2Cl^- - 2e^- \rightarrow \overline{Cl}_2 \\ \text{Cathode: } & \underline{Zn^{2+} + 2e^- \rightarrow Zn} \\ \text{Cell: } & \quad Zn^{2+}Cl_2^- \rightarrow \underline{Zn} + \overline{Cl}_2 \end{aligned}$$

In order to avoid confusion, equations representing electrolysis should always be labeled as indicated above.

19.3. Some Broad Aspects of Electrolysis

The electrolysis of aqueous zinc chloride solution serves as a suitable basis for the consideration of a number of features common to all situations of this general type. These are enumerated in terms of summarizing statements followed by some necessary explanatory remarks and illustrations.

1. **The occurrence of electrolysis requires the utilization of an outside source of electrical energy.** The chemical changes that occur during electrolysis involve an accompanying transformation of